

# RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XIV

NUMBER 3



*July, 1941*

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DIVISION OF RUBBER CHEMISTRY  
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# RUBBER CHEMISTRY AND TECHNOLOGY

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Entered as second-class matter April 28, 1939, at the Post Office at Baltimore, Maryland, under the Act of August 24, 1912. Acceptance for mailing at special rate of postage provided for in the Act of February 28, 1925, embodied in paragraph 4, Section 538, P. L. and R., authorized September 25, 1940.

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## RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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## TECHNOLOGISTS NEEDED BY THE GOVERNMENT

The U. S. Civil Service Commission has announced an open competitive examination to secure Technologists for National Defense work. Difficulty is being experienced in filling positions in such branches of technology as explosives, fuels, plastics, rubber, minerals, and textiles. Persons qualified in these branches are particularly urged to file application. Applications will be rated as received until *December 31, 1941*.

The duties of the positions include the planning, conducting, and reporting of investigation or research in some specialized branch of technology such as explosives, fuels, plastics, rubber, minerals, and textiles; or the testing, designing, or manufacturing of the materials essential for the successful operation of an industrial plant where such plant operation is based on some specialized branch of technology. Applicants must have completed a 4-year college course with specialized major study except that they may substitute, year for year, for the required education, professional experience in the appropriate fields of science, engineering, or technology. In addition, applicants must have had a certain number of years of professional experience in appropriate fields, the number of years varying with the grade of technologist; graduate study in an appropriate field may be substituted for a part of this experience.

The positions to be filled are in several grades with salaries ranging from \$2,600 to \$5,600 a year. Competitors will not be given a written test but will be rated upon their education and experience.

Further information and application forms may be obtained from the Secretary of the Board of U. S. Civil Service Examiners at any first- or second-class post office, or from the United States Civil Service Commission, Washington, D. C.

## NEW BOOKS AND OTHER PUBLICATIONS

RUBBER AND ITS USES. Harry L. Fisher. Published by Chemical Publishing Co., Inc., 234 King St., Brooklyn, N. Y. 1941. Cloth, 5½ by 8½ inches, 128 pages. Indexed. Price \$2.25.

Here is a book that the uninformed can read quickly and obtain a clear picture of what rubber is, what is its history, where it comes from, how it is obtained, and how it is manufactured into the many articles of daily use. As

the author points out, the volume grew out of his experiences, during 17 years as a rubber research chemist, in lecturing before many different groups. The intent is to tell this story of rubber in a volume that can be read in one sitting. In consideration of the imposed brevity of treatment, the amount of information packed within the book's pages is amazing.

After sketching the history of the rubber industry, succeeding chapters in the book deal with: the sources and production of crude rubber; the properties of crude and vulcanized rubber, and the importance of vulcanization; compounding and vulcanizing; manufacturing rubber; latex-manufacturing processes; synthetic rubbers or elastomers; rubber derivatives. A list of reference works for supplemental reading is included. Not only will the uninitiated profit from this book, but those connected with the rubber industry should find pleasure in a book which so clearly explains this difficult subject. [From the *India Rubber World*.]

**RUBBER: LIST OF PUBLICATIONS** by Members of the Staff of the National Bureau of Standards. LC-634 superseding LC-532. National Bureau of Standards, Washington, D. C. 18 pages.

This list, brought up-to-date and covering all publications on rubber by members of the Bureau's staff, includes the following subjects: general information; latex and crude rubber; purification of rubber; forms of rubber; crystallization and other transitions; constants and properties of rubber and isoprene; chemical analysis; dimensional measurements on rubber specimens; physical testing; products; specifications; commercial standards. The papers listed have appeared in Bureau publications and in various scientific and technical journals. [From the *India Rubber World*.]

**ABSTRACTS OF PATENTS RELATING TO RUBBER LATEX.** Compiled by T. R. Dawson and R. W. Parris. Published by the British Rubber Publicity Association, 19 Fenchurch St., London, E.C. 3, England.  $5\frac{1}{2} \times 8\frac{1}{2}$  in. 136 pp.

The last edition of "Rubber Latex", the booklet which treats of the source, production, treatment and application of latex, first issued in July, 1928, by the Rubber Growers Association, whose promotion activities are now in the hands of the British Rubber Publicity Association, contains a summary of British patents ending with No. 438,795. A survey of these patents covering the series from December 19, 1935 to May 17, 1940, resulted in the collection of approximately 800 specifications dealing with the treatment and applications of latex. Abstracts of these additional specifications are included in the present volume, which is issued as a supplement to the last edition of "Rubber Latex", issued in April, 1936.

Like editions of the parent book, the supplement has complete author and subject indexes, compiled mainly in relation to the articles made, or to the methods and processes used, so that essentially they are indexes for users of latex. An American edition of "Rubber Latex" is available from the Chemical Publishing Co., Inc., 234 King Street, Brooklyn, N. Y., at \$2.00 per copy. [From *The Rubber Age* of New York.]

**PATENT FUNDAMENTALS.** Leon H. Amdur. Chemical Publishing Co., Inc., 148 Lafayette St., New York, N. Y. 1941. Cloth,  $5\frac{1}{2} \times 8\frac{1}{2}$  inches, 305 pages. Index. Price \$4.

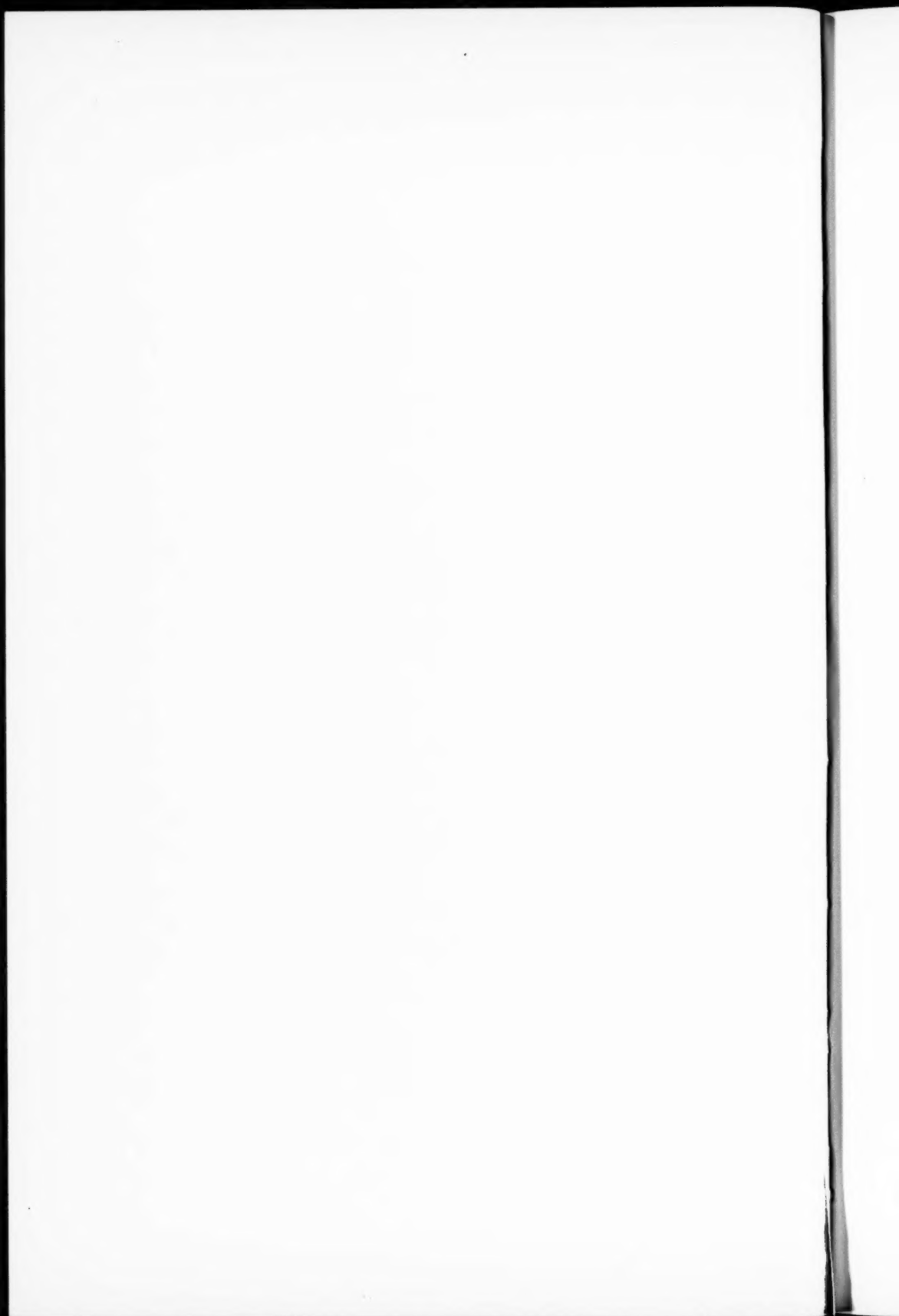
This book, written in understandable language, has two major purposes: to enable the layman and the student to attain a rapid, yet sound, understanding of the U. S. Patent System; and to provide those already versed in the intricacies

of patent law with interesting and helpful information. The book tells what can be patented and what constitutes invention, discusses the nature of a patent, and explains how patents are classified and how patent searches are conducted. Also explained are the function and drafting of patent claims, assignments and licenses, shop-rights, and other pertinent subjects. [From the *India Rubber World*.]

PLASTICS IN INDUSTRY. By "Plastes". Published in England. Available from Chemical Publishing Co., Inc., 234 King St., Brooklyn, N. Y.  $5\frac{1}{2} \times 8\frac{1}{2}$  in. 241 pp. \$5.00.

This is a full and frank discussion of plastics, with as much attention given to its disadvantages as to its more numerically advantages. It has been compiled primarily for industrialists with the object of clarifying many confused ideas regarding plastics and the plastics industry. The authors, writing under the name of "Plastes", decry the sensationalism which has accompanied the growth of the industry, and set forth clearly a real picture of the potentialities and limitations of plastics, believing such a true picture is essential to the well-being of the industry.

First defining the various types of plastics commercially available, the authors then discuss specifications, moulding and fabrication technique, and engineering and chemical machinery and equipment, following which they devote several chapters to explaining the use of plastics in specific industries, including the electrical, aircraft, automotive, textile and building fields. One chapter is devoted to "Synthetic Rubber in Modern Industry", although the authors take the stand that these compositions should be called rubberlike plastics, rather than synthetic rubbers. The book includes thirty-two excellent illustrations, several diagrams and charts, and a subject index. [From *The Rubber Age* of New York.]



# PHASE TRANSITIONS IN RUBBER AND THEIR CONNECTION WITH THE STRESS-STRAIN CURVE \*

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## 1. INTRODUCTION

In a series of recent papers it has been shown that the elasticity of long-chain compounds can be fairly well explained by assuming that a difference of entropy, rather than of energy, distinguishes the extended from the relaxed state<sup>34, 57, 76, 96, 97, 98</sup>. In other words the contractile or kinking tendency of a rubberlike molecule is due to random thermal motion of its segments, rather than to an orienting force at each bond. In this respect, the stretching of rubber is to a certain extent analogous to the compressing of a gas, resistance to which process is due to random kinetic motion of molecules, and not to repulsive forces among them. In ideal rubber, as in an ideal gas, elasticity would be entirely due to such entropy changes; in real gases and real rubbers, there are appreciable changes in potential energy among the kinetic units (molecules in one case, chain-segments in the other). Indeed, simple kinetic mechanism plays the overwhelming rôle only during the first 100 or 200 per cent of the extension curve, and later on shares importance with the process of crystallization. The entropy effect is useful in understanding the initial modulus of elasticity, and in evaluating its absolute value and temperature dependence, but a more intimate study of the extension curve makes it necessary to visualize and describe more adequately the crystallization of rubber and other long-chain molecules.

An attempt has been made to follow the conditions prevailing during crystallization by a simple application of the Clausius-Clapeyron equation<sup>36, 67</sup>. It has been shown that this leads to the right order of magnitude for the heat of fusion of rubber crystallites or micellae. However, this treatment can be regarded only as a very rough first approximation, and it seems necessary to consider more thoroughly the process of formation of rubber crystals from the amorphous phase. It cannot be pretended that at present one is already in a position to give a complete picture of this order-disorder transition, but there is enough experimental evidence to justify a somewhat detailed discussion of the problem<sup>1, 8, 9, 29, 72, 99</sup>. A few features of such crystallization processes will be pointed out, and correlated with the behavior of rubber at higher elongations namely, above 100 per cent extension.

## 2. PHASE RULE CONSIDERATIONS

The equilibrium of a two-phase one-component system is governed by the Clausius-Clapeyron equation in its simple form.

$$\frac{dT}{dP} = \frac{\Delta V}{\Delta S} \dots\dots\dots (1)$$

\* An original contribution.



This requires that the material have a sharp melting-point curve, as shown in Figure 1, where the melting points of low-molecular substances are given as a function of pressure. The dependence of the melting point of rubber on the tension should be expressed by an analogous sharp curve, if rubber could be considered as a simple one component system. At a given stress, where the crystalline and amorphous phases are in equilibrium, a slight temperature rise should result in complete melting, and a slight temperature decrease in complete crystallization. There is no experimental evidence of any such property. Instead, the melting of rubber always takes place over a range of conditions. x-Ray studies carried out by Susich<sup>1</sup>, Clews and Schossberger<sup>11</sup>, Clark<sup>8</sup>, and Gehman<sup>27</sup>, all show that if a rubber sample is kept under a given stress, an increase of temperature results in a limited decrease in the proportion of the crystalline phase. Even after a very long time, the situation does not change. This lack of sharpness in melting point might be interpreted as a sign that equilibrium has not been reached; that one has a supercooled liquid or a superheated crystal.

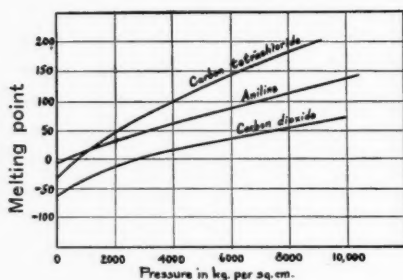


FIG. 1.

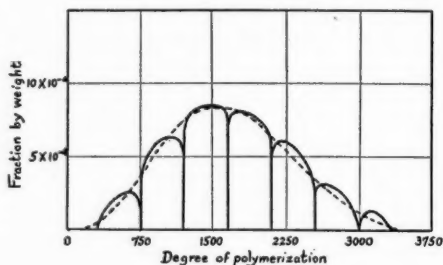


FIG. 2.

This, however, seems improbable if one considers that the velocity of crystallization is high. Davey<sup>12</sup> has shown that at room temperature rubber within less than a minute after stretching shows the usual well known x-ray diagram, with no subsequent change during the next hours. At low temperatures, of course, crystallization is not so rapid. If we take x-ray diagrams to represent equilibrium conditions, as such experiments suggest, it becomes plain that rubber cannot be adequately treated as a simple one-component system.

Several explanations for the vagueness of the melting curve of rubber present themselves, and will be discussed separately.

- (1) a distribution of molecular chain length.
- (2) a distribution of elementary kinetic units.
- (3) an interaction of the growing crystals.

(1) Systems of two or more components exhibit, in general, melting ranges, rather than sharp melting points. Since rubber is known to be made up of molecules which are not identical in chain length, one may be tempted to ascribe the unsharp melting point of rubber to the multi-component nature of the material. It would be possible, for example, to consider rubber as a mixture of many fairly homogeneous fractions, as indicated in Figure 2. Unfortunately, if we apply ordinary thermodynamical considerations to such a mixture, we are still unable to explain the observed properties of rubber. It is true that, in general, such mixtures exhibit melting ranges rather than sharp melting points.



However, the variation of crystalline content with temperature would be expected to follow a curve similar to one of those in Figure 3a. Actually, the curve for rubber is quite different in nature, as shown in Figure 3b.

The reason for the failure of such a treatment lies in the fact that there is a fundamental difference between the crystallization of long-chain compounds and the crystallization of a material made up of small molecules. Modern studies show that the crystallites in high polymers are not made up of entire linear macromolecules, but of parts of them<sup>19, 56, 59, 60</sup>. A succession of isoprene units from a given long chain may be lined up as part of one particular crystallite; at the point where this crystallite ends, the molecule will extend on into an amorphous area. Still another section of the same chain may lie in another crystallite, and so on. In materials of ordinary molecular weight, the molecule itself can be considered as the kinetic unit, which is definitely in one of the phases

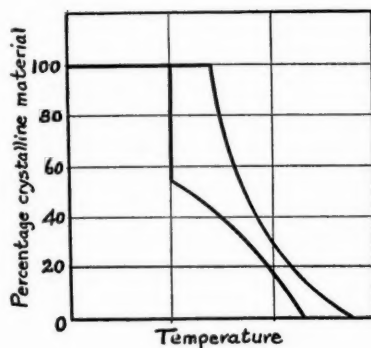


Fig. 3a.

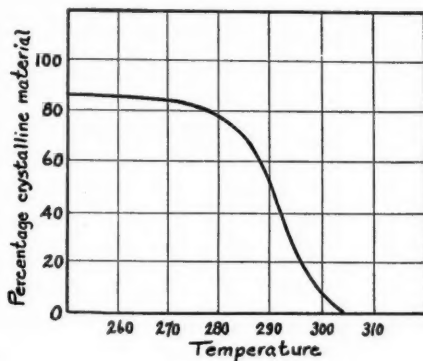


Fig. 3b.

under consideration. High polymers must be thought of, not as a case of distribution of molecules among phases, but rather as a case of distribution of phases among molecules. Meyer<sup>71</sup>, Eyring<sup>19</sup>, Kistler<sup>56</sup>, Fuoss and Kirkwood<sup>24</sup> and Kuhn<sup>60</sup> have shown that segments of high-polymer molecules move about more or less independently of each other, and that such independent segments rather than the molecules themselves, should be considered the kinetic units for any statistical treatment in the concentrated state. The behavior of a given segment in entering or leaving a crystalline phase does not depend to any great extent on the total length of the molecule of which it is a part. It cannot be said, therefore, that the melting range of rubber can easily be explained on the basis of molecular inhomogeneity.

(2) The melting points of normal hydrocarbons are linear functions of the number of carbon atoms for low molecular weights, but for high molecular weights they approach limiting values (see Figure 4) asymptotically<sup>26</sup>. This has been interpreted by Eyring<sup>19, 65</sup> on the assumption that, in sufficiently long chains, individual segments of a molecule act as the kinetic units. In short chains, the motion of a given segment is not independent of the rest of the molecules; here the kinetic unit is the molecule itself. In long chains, however, a given link is not influenced by the local motion of more than about 30 or 40 of its nearest neighbors. The nature of viscous flow in molten high polymers<sup>56</sup>, the osmotic behavior of concentrated polymer solutions<sup>71</sup>, and other experimental

facts<sup>19</sup> all lead to the concept of independently-acting chain segments. In the case of rubber, the length of these independent kinetic units was found by Meyer to be about 40 atoms. This should be true, whether the segment under consideration is part of a molecule of 1000 or of 2000 carbon atoms. From this point of view, the melting point of a linear high-molecular-weight material such as rubber should depend only on the nature of the repeating structural unit (which determines the forces between the chains), and not on the total chain-length. If the kinetic unit were sharply defined as to size, one would expect rubber to possess a sharp melting point. However, it would be an obvious oversimplification to say that a given methylene group behaved as if it belonged to an independent kinetic unit of exactly 30 or exactly 40 members. The local geometrical and dynamical conditions will bring with them a certain vagueness in

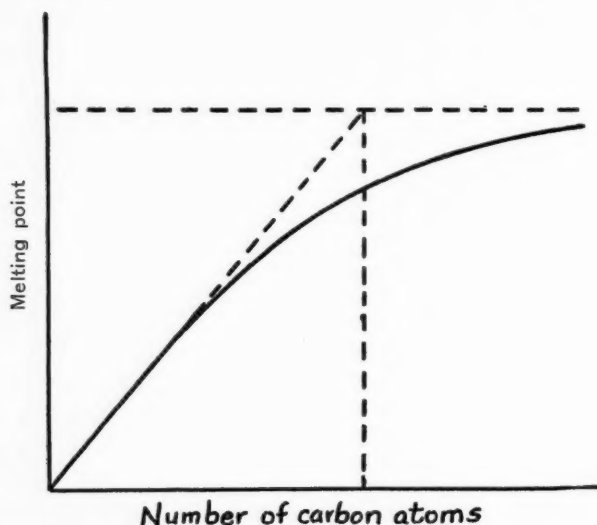


FIG. 4.

the definition of these segments. Thus an improved description of the kinetic behavior of a high-polymer molecule should consider it as the superimposed behavior of segments of somewhat different lengths acting as independent kinetic units. The predominant units are those in the range between 30 and 50 links. Eyring considers his estimate of 40 only as an average size of this unit. The motion of any methylene group, and thus the size of the dominant kinetic units of which it is a part, depends not only on the internal structure of the molecule, but also on the immediate geometrical environment of the group.

If the unsharpness of the melting point of rubber is due to such a distribution in length of effective kinetic units, rather than to the distribution in length of whole molecules, then even a fraction of rubber in a narrow molecular weight range should show the same unsharpness of melting point as ordinary rubber. The only change would be caused by the removal of the very low-molecular-weight material, to which such a treatment would not apply.

Such a distribution of effective kinetic units not only explains the melting range of rubber, but also fits in with the plasticity of high polymers, as discussed

by Kistler<sup>56</sup>, with the viscosity of fused polymers<sup>19</sup>, with the osmotic behavior in concentrated solutions<sup>71</sup>, and with the dielectric properties of polar high-polymers, as studied by Fuoss, Kirkwood and Busse<sup>7, 24</sup>. All these results point to an interpretation of the kinetic behavior of long-chain molecules in concentrated systems which is based on the response of independent segments, rather than of whole molecules, to environmental changes. Kirkwood and Fuoss in particular find a distribution of relaxation times corresponding to a size distribution of relaxing segments.

(3) In many thermodynamical problems, surface effects may safely be ignored. In the case of high polymers however, the crystallites are so small that the surface energy may be an appreciable fraction of the total. Among such tiny crystals, a marked inhomogeneity in size could of itself explain a certain amount of unsharpness of the melting curve, since the melting point of the very smallest crystals would be different from that of the larger ones. However, x-ray studies seem to indicate that the rubber crystallites are reasonably homogeneous with respect to particle size<sup>8, 9, 28, 29, 39, 69</sup>. It is not likely that ordinary surface effects could explain the range of melting actually observed. Further, the effect of ordinary surface energy would be to make the very smallest crystallites less stable than the larger ones. This would hinder the formation of crystal nuclei, but would not prevent their growth. The surface energy of nuclei is undoubtedly a contributing factor in the determination of rates of crystallization, but examination shows that it can hardly explain the equilibrium melting range of rubber.

On the other hand, the long-chain nature of rubber molecules results in surface effects of a more complex type than the interphase surface energy which is ordinarily encountered. The fact that single molecules may extend from one crystallite to another opens the possibility of mutual crystal interference as an important contributing factor.

It is well known, in the case of metals, that the shape of crystal grains in a quenched melt is determined not by the natural crystalline structure, but by the random manner in which growing grains meet each other and restrain further growth. In the case of rubber, such interaction probably sets in long before two growing crystallites actually meet. Both crystallites may contain segments of common molecules and, in general, the alignment of one crystal will prevent the complete growth of the other. This interference would begin as soon as the crystallites were formed, and would become more and more pronounced as they grew toward each other. This would result, not in a shape restriction, as in the case of metals, but in a vagueness of melting point. Each successive group is less easily fitted into the crystal lattice. This is because crystal growth limits not only the mobility of the entering group, but also the mobility of the amorphous hydrocarbon chain connecting the two crystallites. The change in energy  $\Delta H$  is the same for the last link as for the early ones, but the change in entropy  $\Delta S$  is greater for the later groups. In addition to the entropy decrease or loss of randomness, due to the fixing of the group, which actually enters the lattice, there is an associated decrease in the randomness of the amorphous connecting chain, due to the choking action of the two growing crystallites. This mechanism would, of course, lead to the sort of unsharp melting point at given tension which is observed experimentally.

This suggested explanation is a kinetic picture of the point of view expressed in thermodynamical terms in the previous section, *i.e.*, that the properties of rubber are best explained by the assumption of a distribution of kinetic units.

According to Garner and King<sup>26</sup>, the energy difference  $\Delta H$  between normal

hydrocarbon chains of medium length in the crystallized and molten state is given by:

$$\Delta H = q_0 + n \cdot q \dots \dots \dots (2)$$

In this expression  $n$  stands for the number of methylene groups,  $q$  is the heat of fusion per methylene group (order of magnitude of 1000 calories per mole) and  $q_0$  is the influence of the end groups, which is negligible as soon as  $n$ , exceeds five or six.

The entropy change,  $\Delta S$ , is given by another equation:

$$\Delta S = s_0 + s(n) \dots \dots \dots (3)$$

in which  $s_0$  gives the entropy gain, owing to the fact that the centre of gravity of the whole molecule is set in freedom (macro-Brownian movement of Kuhn), while  $s(n)$  is a function which represents the increase of randomness, owing to the fact that, on melting, the chains acquire their full internal mobility (micro-Brownian movement of Kuhn).

Since Equation (2) represents a simple proportionality the energy change is identical for each link, while (3) has a more complicated form and therefore the entropy change per group is less for long molecules, whereas the energy change per group is the same for all molecular lengths. If we apply this analysis to the kinetic units which act in the crystallization of rubber, where the choking action of growing crystallites results in an extra entropy decrease for the later groups, the last groups to enter the lattice can be interpreted as being members of kinetic units smaller than those which dominate in the case of the first groups. Thus the statement above that the "lengths of the effective kinetic units depend, not only on the internal structure of the molecule, but also on the immediate geometrical surroundings of any particular section of the molecule" is merely a more general expression of the mechanism postulated here; *viz.*, that the interaction among growing crystallites makes it more and more difficult for each subsequent group to line itself in the lattice.

After these remarks concerning the influence of the long-chain nature of rubber on its crystallization, it may be appropriate to discuss a little more fully the nature of the equilibrium between the two phases, on the basis of the postulated mechanisms of kinetic unit distribution and crystal interaction.

When a piece of rubber is stretched, the effective kinetic units respond (time of relaxation below  $10^{-3}$  seconds) to their immediate environments, and relax into the equilibrium configurations demanded by those immediate configurations (micro-Brownian movement). In this case a still more stable state would, in general, exist. This change would involve the relaxation of whole molecules into their equilibrium configurations. This more thorough-going change, however, would have a considerably larger time of relaxation (above  $10^4$  or  $10^5$  seconds), and would not take place to any observable extent during a normal extension experiment. Therefore, from the standpoint of effective kinetic units, and based on their immediate surroundings, the actual state is the equilibrium state. On the other hand, from the standpoint of whole molecules, the actual state is not that of equilibrium, for the rate of attainment of the more fundamental equilibrium is slow. This is easily seen in the case of rubber which has been crystallized to the maximum possible extent. The postulated crystal interaction would mean that the intermicellar amorphous chain-segments would be nearly as constrained as in the crystallite phase, without having been compensated by a more favorable energy state. It is clear that a more stable state would be represented by a completely aligned configuration, with no strained amorphous connec-

tions. This would be a single crystal. However, the change to such a configuration would involve the extremely slow transport of entire molecules. From the molecular standpoint, then, the most highly crystallized rubber is still a supercooled system which is not in equilibrium; but from the standpoint of the effective kinetic units, it is an equilibrium system. As long as we consider the kinetic behavior of rubber from the standpoint of these units (which involves the behavior of the sample in times not longer than  $10^4$  seconds), an equilibrium treatment may be justified, just as the interdiffusion of two chemically reactive gases can be considered as the attainment of an equilibrium state in which the gases are mixed, but unreacted.

If rubber is cooled rapidly to a very low temperature, even the relaxation of the (room temperature) kinetic units into their equilibrium configurations (micro-Brownian movement) may be prevented. Thus when a piece of rubber or a synthetic high polymer is dipped into liquid air, it becomes very hard, but gives no x-ray crystal diagram. Such a sample is in a supercooled state, not only from the standpoint of whole molecules, but also from the standpoint of segments of 30 to 40 links. Very interesting investigations as to the exact influence of time and temperature on the crystallization of rubber are being carried on by Bekkedahl and Wood<sup>1, 2, 99, 100</sup>.

Flow hysteresis might be described as the process of attaining a more fundamental equilibrium state, by the relaxation of larger, less mobile kinetic units than those which determine the crystallization curve.

### 3. RECENT EXPERIMENTAL WORK ON THE CRYSTALLIZATION OF RUBBERS

Until fairly recent years, experimental investigations of the physical properties of rubber have been far from satisfactory. The various properties were often measured in an isolated fashion, and few studies were made to correlate all the physical constants, with their temperature variations, for the same sample. The extensive research program now being carried on by Bekkedahl, Holt, McPherson and Wood at the National Bureau of Standards<sup>1, 2, 3, 47, 99, 100</sup> is providing much of the information which has been so long needed. It is now possible to present a fairly reliable set of values for most of the physical constants of rubber. Figures 5a to 5d present the values of the enthalpy, specific volume, heat capacity, and coefficient of expansion, as functions of the temperature, both for amorphous and crystalline rubber. The crystalline rubber of these figures is not, of course, a material of 100 per cent crystalline content, but still contains a certain proportion (5 to 10 per cent) of the amorphous form.

Figures 5a to 5d indicate two distinct transition points in rubber—a second-order phase change at  $-70^\circ\text{C}$  and an anomalous first-order change (the melting of rubber crystallites) at about  $11^\circ\text{C}$ .

A normal first-order transition point is characterized by a sudden change in the values of the energy, specific volume, or entropy at a definite temperature. The first derivatives of these quantities (heat capacity, coefficient of expansion, etc.) momentarily become infinite. The melting of rubber involves a sudden change in specific volume, energy, and entropy—not at a single temperature, but within a fairly narrow range. This process is, therefore, an unsharp first-order phase change. It was postulated earlier that the explanation of the unsharpness of the melting point of rubber lay in the mutual interaction among growing crystallites. The increasing constriction of the amorphous intermicellar segments makes it progressively more difficult for each successive unit to enter the lattice.

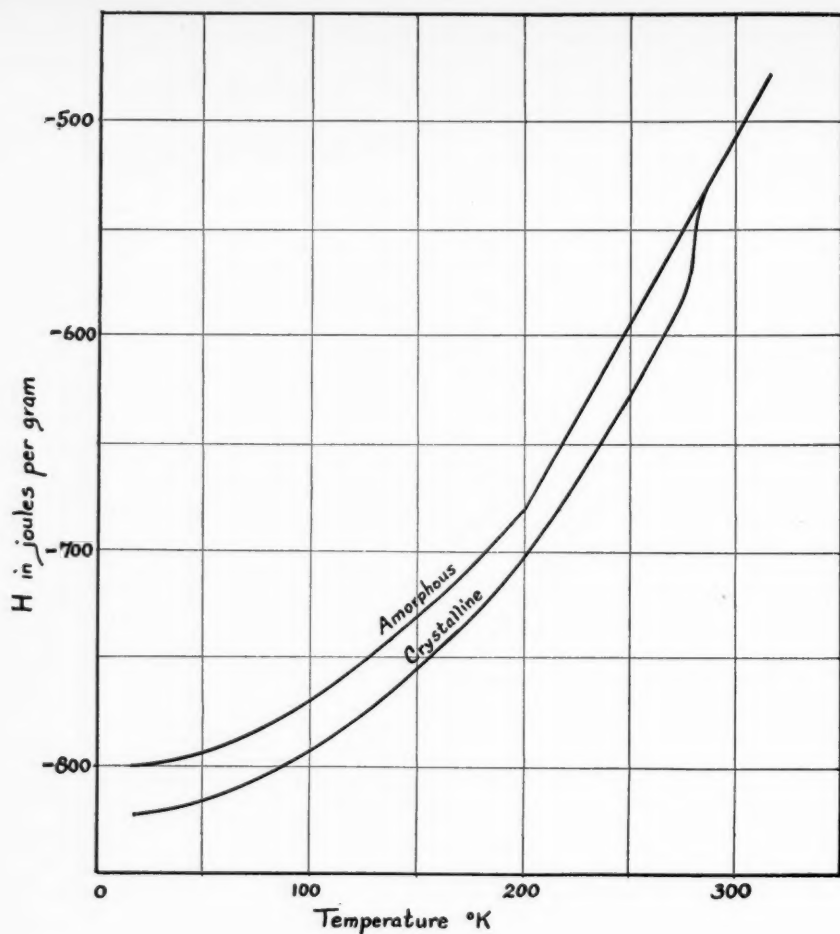


FIG. 5a.

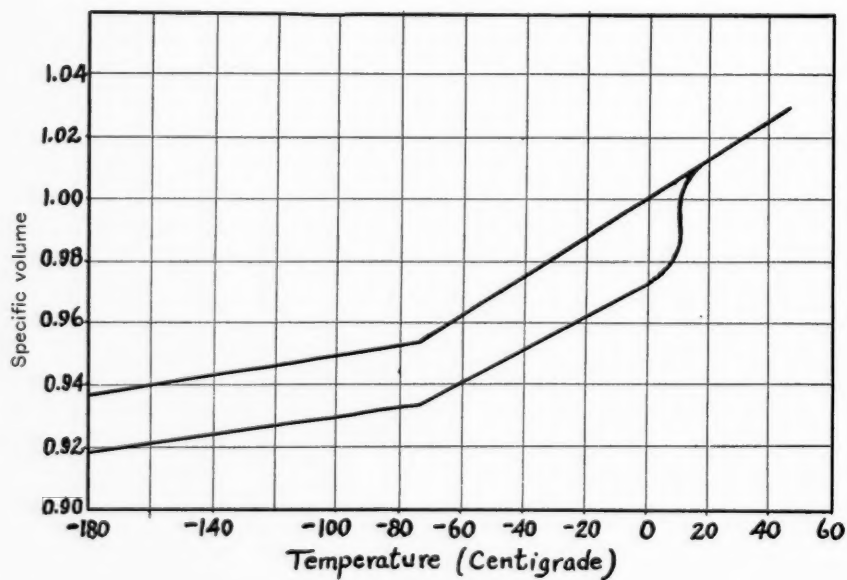


FIG. 5b.



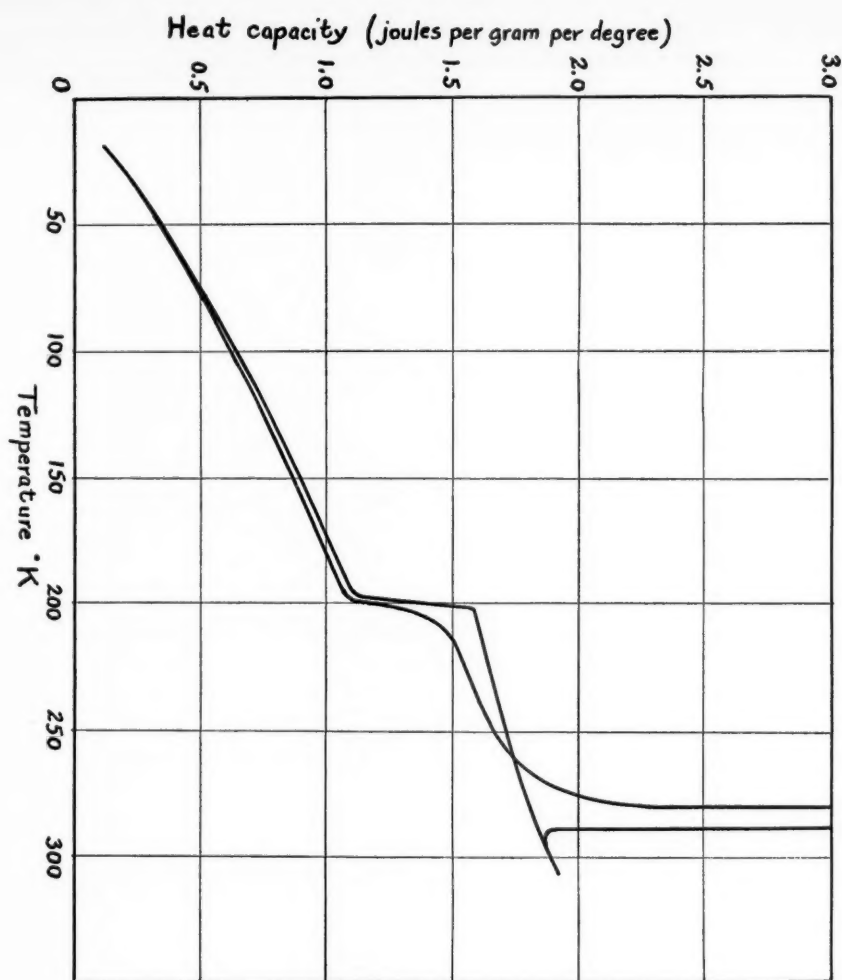


FIG. 5c.

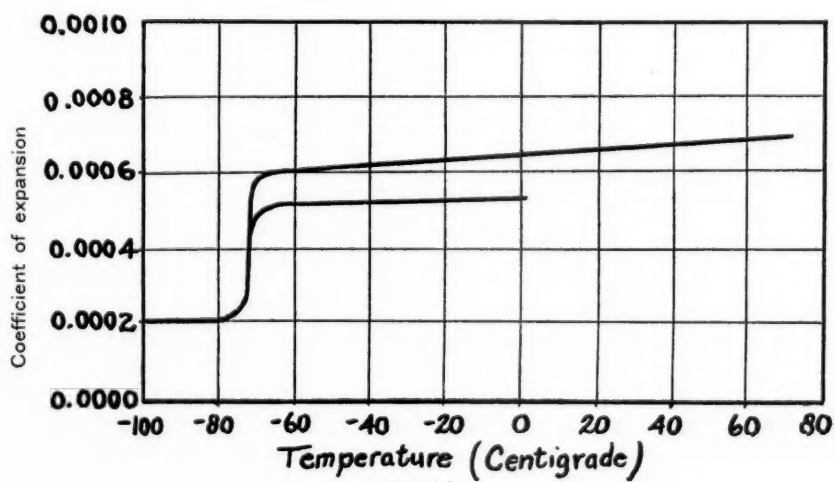


FIG. 5d.

The transition occurring at  $-70^{\circ}\text{C}$  is a phase change of the second order. The primary thermodynamic variables experience no discontinuity of magnitude, but only of slope. The first derivative variables (coefficient of expansion, heat capacity, etc.) jump suddenly to higher values, and the second derivative variables, if plotted, show temporary values of infinity. It is most significant that this second-order transition takes place at nearly the same temperature for both amorphous and crystalline rubber, and that, below the transition point, the two forms are practically indistinguishable with regard to coefficient of expansion and heat capacity. A fairly probable explanation of such data is that the molecular chains become free to rotate at this temperature. Since the immediate environment of any isoprene group is much the same in the amorphous as in the crystalline state, this micro-Brownian rotational movement should come into play at the same temperature for both forms. This explanation of the transition is in accord with independent x-ray studies of other long chain compounds. Muller has shown that paraffins and their derivatives<sup>78</sup> show second-order transition points, at which there is a change from a lattice made up of elements of elliptical cross-section to one with elements of circular cross-section. This would correspond to the change from rigidly bound hydrocarbon chains to molecules which rotate freely or nearly freely about their long axes.

Figure 6 shows the specific volume-temperature relationship for several vulcanized samples. It is clear that, in these cases, the second-order transition takes place at higher temperatures for the more highly vulcanized samples. This would indicate that the cross-linking left the chains somewhat less free to rotate.

#### 4. RATES OF PHASE CHANGES

Data such as those presented in the previous section presuppose a careful selection of experimental conditions. Amorphous rubber, for example, is unstable below its melting point, and changes slowly into the crystalline form. Experiments such as those represented by figures 5a to 5d must be carried out rapidly enough for that material under investigation to remain amorphous. Similar rate problems occur so frequently in the investigation of rubber that it may be worthwhile to give the order of magnitude of the rates of various phase changes under different conditions.

Figure 7, taken from a paper of Holt and McPherson<sup>47</sup>, gives a good idea of the rate of crystallization of a rubber sample held at  $0^{\circ}\text{C}$ . Crystallization time is a matter of days. At liquid air temperatures, amorphous rubber can be kept indefinitely without crystallization. Bekkedahl<sup>2</sup> found that crystallization took place most readily between  $-25^{\circ}$  and  $-15^{\circ}\text{C}$ . In this temperature range, the time necessary for crystallization was of the order of hours. When slowly heated from  $-72^{\circ}\text{C}$ , amorphous samples followed the amorphous specific volume-temperature curve (Figure 5b) to about  $-25^{\circ}\text{C}$ . At this temperature, the rubber began to decrease in specific volume, and continued to do so until it reached the volume characteristic of crystalline rubber. During this change, there was a marked evolution of heat.

The reverse transition—melting of crystalline rubber—takes place much more rapidly than crystallization. Crystallized samples, raised to  $25^{\circ}\text{C}$ , melted within the time required for the establishment of a temperature equilibrium.

The limiting factor in the rate of crystallization is very probably the formation of crystal nuclei. Addition of units to a crystal which is already present presumably takes place rapidly. This is indicated both by the S-shaped crystallization curve of Fig. 7, and by another very interesting experiment of Bekkedahl<sup>2</sup>.



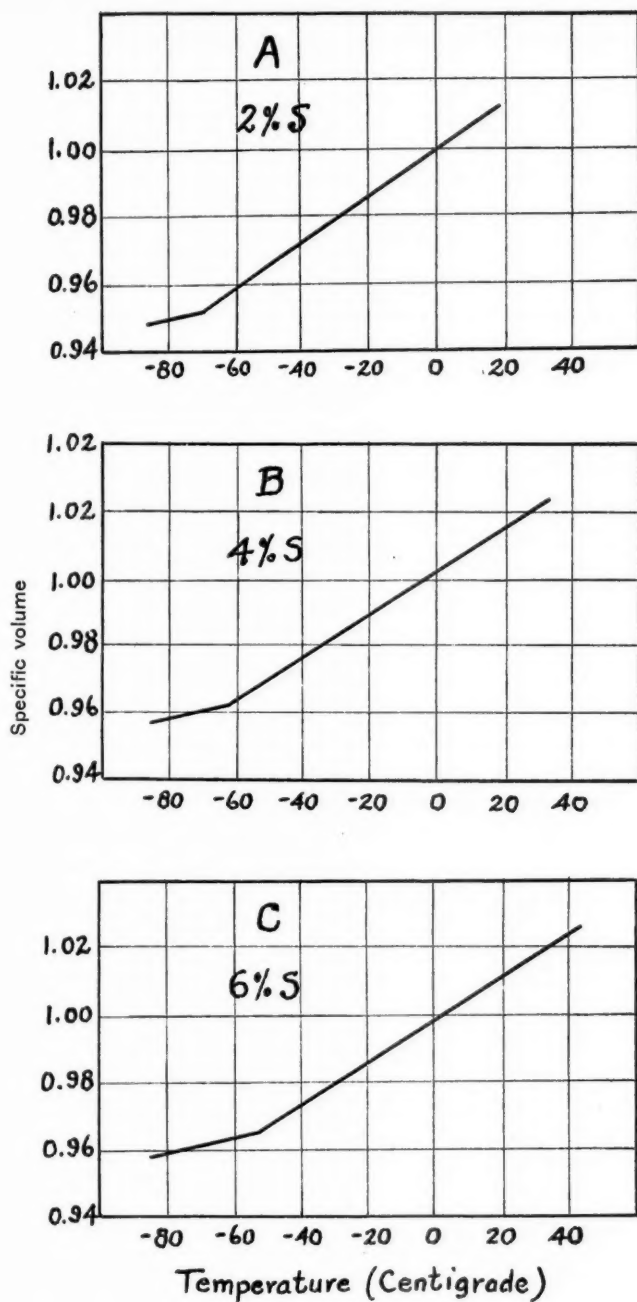


FIG. 6.

When crystalline samples were warmed to 10° C, and subsequently cooled again, the temperature-specific volume relation described exactly the lower curve without lag. At 10° C, a considerable fraction of the crystalline material had become amorphous; unless this amorphous material crystallized quickly on re-cooling, the temperature-volume curve lay above that for the original crystalline rubber. The presence of seed crystallites will be shown to be important also in the case of stretched rubber.

There is no detectable lag in the second-order transition at -70° C for either amorphous or crystalline rubber. This is in harmony with the characteristics of second-order phase changes in general.

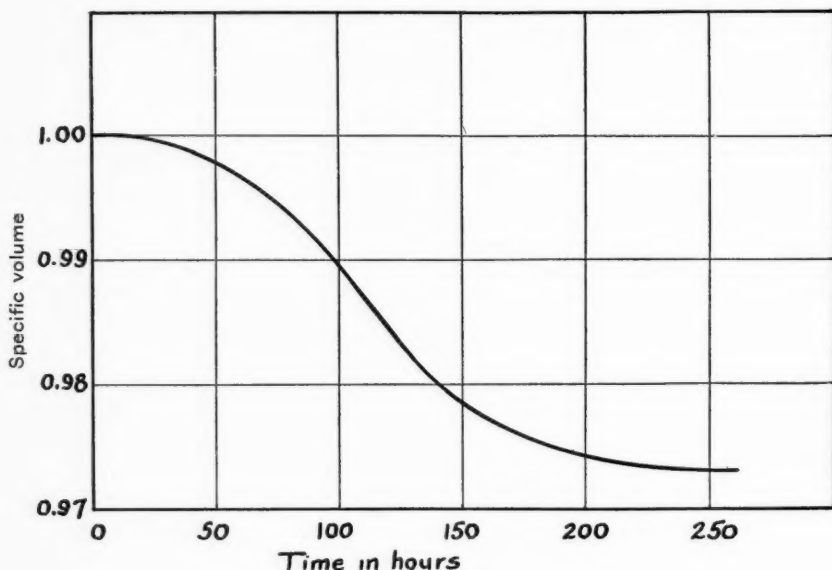


FIG. 7.

#### 5. CHANGES ACCOMPANYING THE EXTENSION OF RUBBER

It is well known, since the discovery by Katz, that stretching promotes the crystallization of rubber, especially in the higher ranges of extension. This effect has recently been studied by Clark and his collaborators<sup>6, 11, 39, 91</sup> by Gehman and Field<sup>27, 28, 29</sup>, and at the National Bureau of Standards<sup>1, 2, 3, 47, 99, 100</sup>. The hydrocarbon chains are straightened out by the continuous stress from their most probable lengths into configurations much more favorable to crystallization. Figures 8a to 8c present data which correlate degree of crystallization with temperature and extension.

It is apparent from Figures 8a and 8b that, at a given temperature, crystallization does not appear until the sample has been stretched a definite amount. Most of the crystallization takes place over a range in the middle portion of the extension curve. Figure 8c shows the effect of temperature on the degree of crystallinity in stretched rubber. Crystallization is favored by high extensions and low temperature.

Rates of crystallization are much higher for stretched rubber than for unstretched rubber. This is indicated by the curves in Figure 9, which give the change in volume of rubber with time after stretching to different elongations at 25° C. On the other hand, there is considerable hysteresis involved in a complete elongation cycle of rubber. Figures 10a and 10b show the stress-strain hysteresis and the crystallinity hysteresis. Fig. 10c shows the volume changes which occur in a stepwise elongation and contraction of a rubber sample.

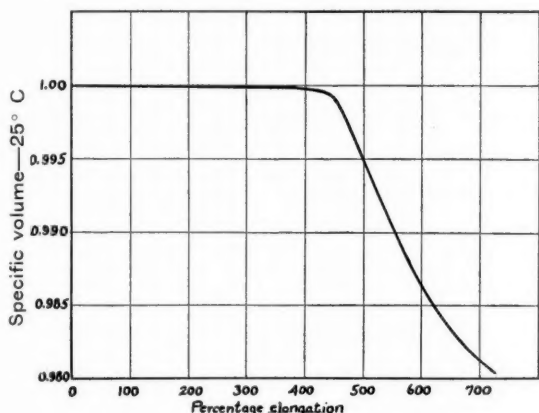


FIG. 8a.

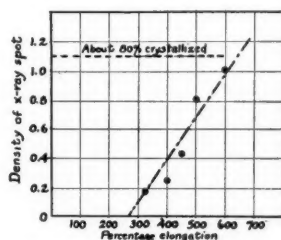


FIG. 8b.

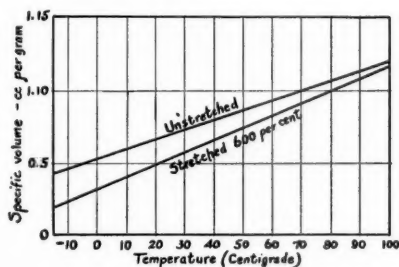


FIG. 8c.

A sample of rubber which has once been stretched exhibits a reduced coefficient of elasticity over the entire extension range when stretched again. This is true even if a long period elapses between the two tests. If the sample is heated for a few minutes to about 60° C, it loses all "memory" of the previous extension and, on subsequent testing, follows the original stress-strain curve. This fact would seem to indicate the presence of crystal nuclei in rubber which has been stretched and then relaxed.

## 6. APPLICATION TO THE EXTENSION CURVE OF RUBBER

It has been pointed out<sup>68</sup> that the extension curve of rubber can be considered as made up of three parts, as indicated in Figure 11a. Early in the process of elongation, rubber exhibits mainly gas-like elasticity. In this range, the entropy

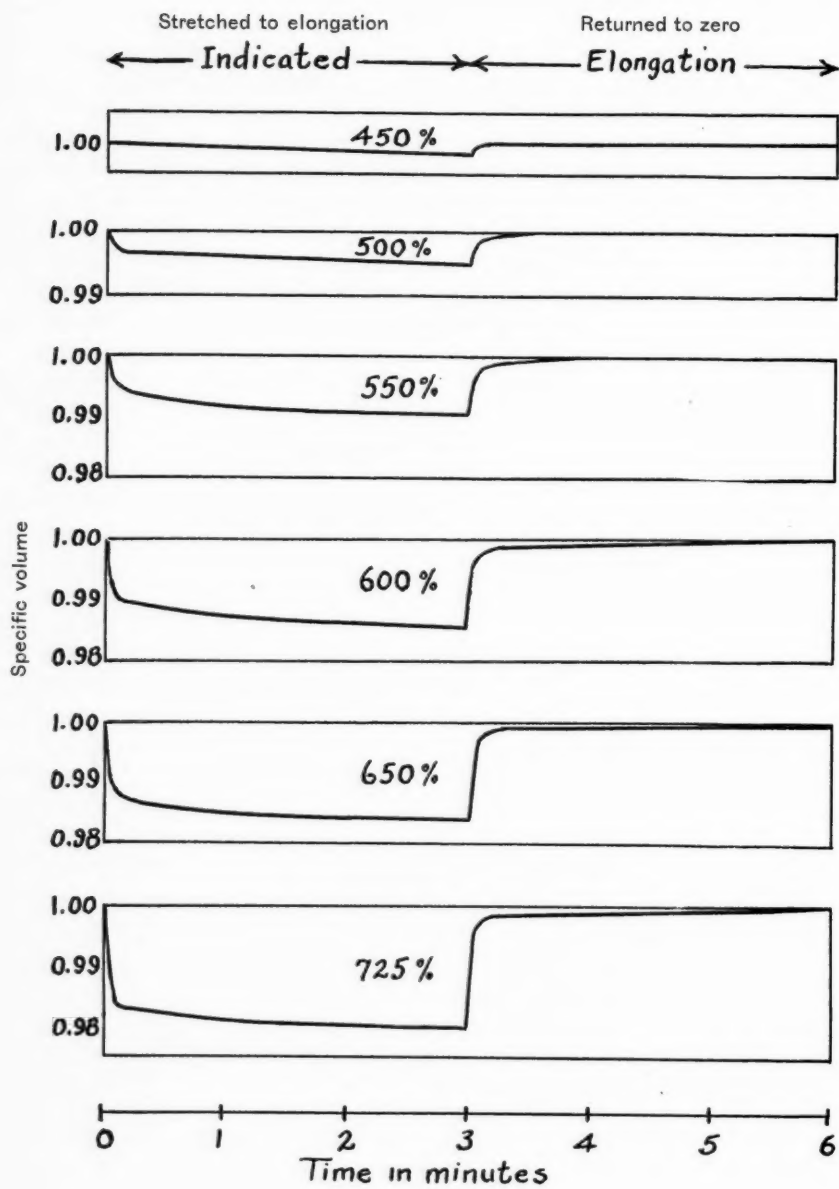


FIG. 9.

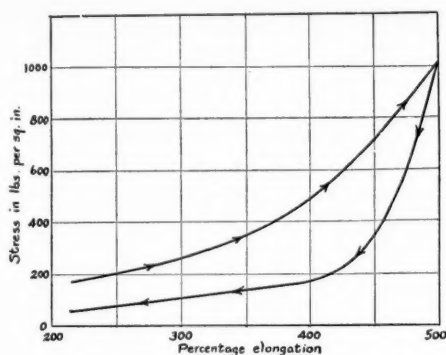


FIG. 10a.

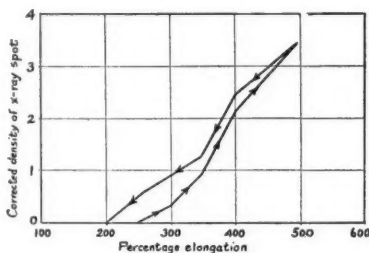


FIG. 10b.

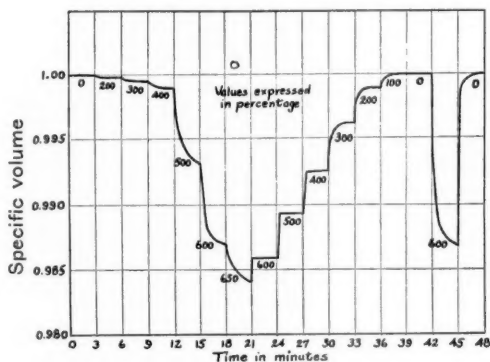


FIG. 10c.

decrease is the predominant factor in opposing extension. In the middle range, the process of crystallization begins to affect the curve, acting in the same direction as the externally applied tension. In this region, the stress-strain curve becomes somewhat flat, since small stresses, aided by the crystallization process, can produce large changes in length. After crystallization has proceeded as far as possible, further extension must involve the stretching of crystallites. In this last range, rubber exhibits the elastic behavior typical of all crystalline substances; high coefficient of elasticity, and small range of extension.

The identification of the S-shaped nature of the extension curve as the effect of crystallization is supported by experimental evidence. Gehman<sup>27</sup> has shown that most of the crystallization of rubber takes place in the intermediate extension range. Furthermore, copolymerized artificial rubbers which do not crystallize do not exhibit the S-shaped extension curve characteristic of natural rubber. Such copolymers as Neoprenes, Buna-S, Buna-N, Ameripol, Chemigum, and Butyl rubber, cannot crystallize so easily as rubber, even when oriented by stretching, since their chains are not made up of identical structural units in a perfectly repeated order.

The phenomenon of spontaneous extension is proof that the crystallization process acts to facilitate the elongation. Gehman and Field<sup>20, 41</sup> have shown that, if a stretched rubber sample is cooled at constant elongation, additional crystal-

lization takes place. The result of this crystallization is to reduce the tensile stress. If cooling is carried far enough, the tension decreases to zero, and becomes a compressive stress. The rubber then elongates without the application of any external tensile stress. Spontaneous elongations as great as 50 per cent of the original (unstretched) length were observed<sup>20, 41</sup>.

A complete theory of rubber extension should predict both the effect of the crystallization process on the apparent coefficient of elasticity and the variation of crystalline content with tension. It is possible, however, to treat the first

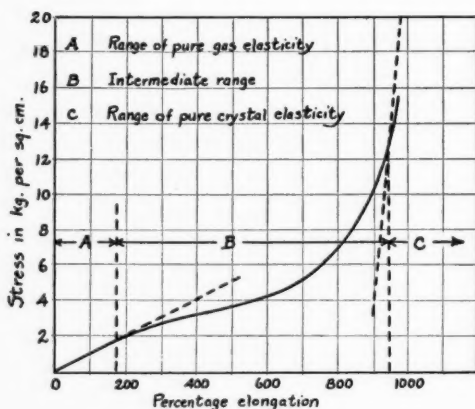


FIG. 11a.

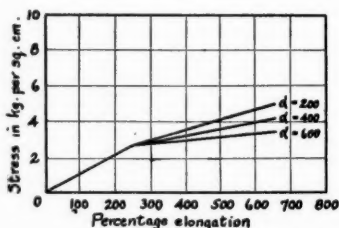


FIG. 11b.

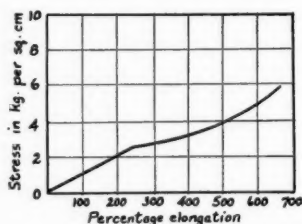


FIG. 11c.

problem by itself, and to correlate, in a rough manner, the extension curve with the experimentally observed crystallization curve. Hauser and Mark,<sup>39</sup> Clark and his coworkers<sup>8, 9, 10</sup>, and Gehman and Field<sup>27, 41</sup> have measured crystallization as a function of elongation. It can be represented in a first approximation as a straight line, starting at about 200 per cent extension. Such a straight-line approximation (as shown in Figure 8b) of the crystallization curve leads to the general shape required of the extension curve.

Let us assume that the dotted straight line in Fig. 8 b approximates closely the actual curve in the region between 250 and 600 per cent elongation. Then  $q$ , the fraction of crystalline material, can be expressed in this range by the relation:

$$q = (\gamma - 250)(0.002) \dots \dots \dots (4)$$

where  $\gamma$  is the elongation in percentage.

If, now, the only effect of the crystallization process is the extra extension, we may write a differential stress-strain relationship as follows:

$$d\gamma = \frac{1}{k} ds + \alpha dq \dots \dots \dots (5)$$

Here  $\gamma$  is the elongation,  $k$  the coefficient of elasticity (gaslike),  $s$  the stress and  $\alpha$  the fractional elongation due to crystallization of 1 per cent of the material. This may be written as:

$$d\gamma = \frac{1}{k} ds + \alpha \cdot 0.002 d\gamma \dots \dots \dots (6)$$

Figure 11b shows a set of extension curves, calculated in the foregoing way, for different values of the constant  $\alpha$ . At the point where crystallization begins, the coefficient of elasticity suddenly changes to a new value.

The crystallization process not only increases the elongation, but also reduces the amount of amorphous phase. In the higher ranges of crystallization, this becomes important, since the quantity of material which can undergo gas-like elastic deformation becomes smaller and smaller. It seems reasonable, therefore, to replace Equation (6) by an expression of the following type:

$$d\gamma = \frac{1}{k} (1-q) ds + 0.002 \cdot \alpha \cdot d\gamma \dots \dots \dots (7)$$

This equation will obviously coincide with Equation (6) for small values of  $q$ . When crystallization has proceeded to a great extent, however, Equation (7) predicts an increase in the coefficient of elasticity. Figure 11c shows the form of stress-strain curve which results from Equation (7).

The sharp break in the above curve results from the assumption that crystallization suddenly begins to take place at 250 per cent extension, and proceeds linearly. This approximation is, of course, not in accord with experimental observations, and a more refined analysis would smooth away the corner on the extension curve.

The differential stress-strain equation could be written in the following more general form:

$$d\gamma = (1-q) \frac{1}{k} \cdot ds + \alpha \frac{\partial q}{\partial \gamma} \cdot d\gamma \dots \dots \dots (8)$$

or

$$d\gamma \left( 1 - \alpha \frac{\partial q}{\partial \gamma} \right) = (1-q) \frac{1}{k} \cdot ds \dots \dots \dots (9)$$

Instead of substituting for  $q$  a linear function of  $\gamma$ , as in Equation (6), it would be possible either to evaluate  $q$  and  $\partial q / \partial \gamma$  directly from experimental curves or to substitute an analytic expression for  $q$  which closely approximates the observed values. Gehman and Field<sup>29</sup> have obtained a distinctly S-shaped curve relating degree of crystallization to extension. However, no experimental stress-strain curves have been made under conditions corresponding to those of their x-ray study. It would, therefore, be of little value to calculate a stress-strain curve based on the finer details of Gehman's curve.

## 7. SUMMARY

This paper reviews recent experimental work on phase transitions in rubber—particularly the change from the amorphous to the crystalline form. Several possible explanations are considered to account for the vagueness of the melt-



ing point of rubber. Molecular inhomogeneity does not completely explain the phenomenon, and a more satisfactory approach involves a size-distribution of effective kinetic units. It is suggested that the reason for such a variation in size of the kinetic units lies in the mutual interference of growing crystallites.

Crystallization of rubber by stretching is discussed, and it is shown that the crystallization process, which takes place mainly in the middle part of the extension, accounts in a reasonable way for the S-shaped nature of the stress-strain curve.

The authors wish to express their deepest appreciation to Norman Bekkedahl and Lawrence A. Wood, of the National Bureau of Standards, with whom they had the privilege of discussing many of the questions involved, and to T. S. Carswell of the Monsanto Chemical Co., who has made it possible for one of us (T. A.) to work at the Brooklyn Polytechnic Institute.

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# INFLUENCE OF THE TEMPERATURE OF CRYSTALLIZATION ON THE MELTING OF CRYSTALLINE RUBBER \*

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Data presented in this communication show an instance in which melting of a crystalline material is very much dependent on the temperature at which the crystals have been formed. It is well known that many substances in which crystallization is relatively slow can be crystallized at different temperatures in a range below the melting point, but no effect of the crystallization temperature on the temperature of melting seems to have been previously reported. The quantitative results for crystalline rubber, the material under investigation, are shown in Figure 1.

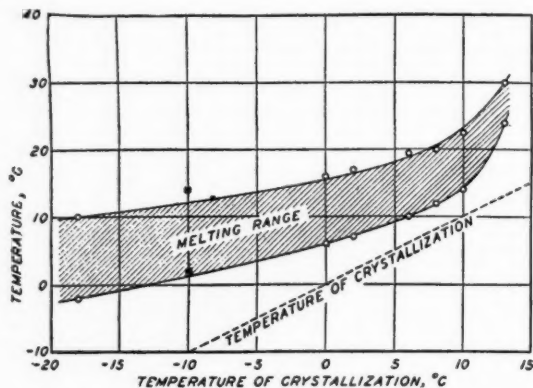


FIG. 1.—Melting range of crystalline rubber as a function of the temperature of crystallization. The lower points represent the beginning of melting, the upper points the ending of melting. The broken curve shows the crystallization temperature as ordinate for easier comparison with the range of melting temperature in each case. Van Rossem and Lotichius.

The crystallization<sup>1</sup> of unvulcanized rubber in the unstretched state has been found to occur at temperatures between about  $-40^{\circ}\text{C}$  and  $13^{\circ}\text{C}$ . The time required for crystallization is about one year at  $13^{\circ}\text{C}$ , about ten days at  $0^{\circ}\text{C}$ , and a few hours at  $-20^{\circ}\text{C}$ . Below  $-40^{\circ}\text{C}$  the mobility is presumably insufficient for the formation of crystals. Crystallization and fusion are accompanied by changes in volume, heat capacity, light absorption, birefringence, x-ray diffraction, and mechanical properties such as hardness. The volume decreases about 2.5 per cent on crystallization, and the magnitude of the change is little influenced, if at all, by the temperature. Fusion, as measured by the volume increase, is found to be independent of the rate of heating, and to occur over a range of five or ten degrees.

\* Reprinted from the *Journal of Chemical Physics*, Vol. 9, No. 2, page 193, February 1941.

In the present work, volume change, as measured in a mercury-filled dilatometer, was taken as the criterion of crystallization. Smoked sheet rubber was held at various fixed temperatures until no further volume change could be detected. After each crystallization the temperature was raised, and observations were taken for a graph of the volume as a function of temperature. The temperature corresponding to the beginning of melting could be located as that at which the observations began to deviate from the curve representing the normal thermal expansion of crystalline rubber. Likewise, at the end of the melting range the observations began to follow the curve representing the normal thermal expansion of amorphous rubber. These two limiting temperatures could be located within about one-half a degree, and are plotted in Figure 1. The shaded area between the curves represents the melting range.

It is to be observed from the figure that the higher is the temperature of crystallization, the higher are the temperatures at which both the beginning and ending of melting occur. The range of melting itself appears to become somewhat narrower at the higher crystallization temperatures. From the fact that the broken curve does not intersect or touch the shaded area, it appears that there is no temperature at which crystalline and amorphous rubber are in equilibrium at atmospheric pressure. If the crystallization occurs between about 6° and 10° C, melting of the crystals begins at a temperature about 4° above that at which the crystals were formed. This interval is greater than 4° for crystallization at temperatures above or below this range. In previous work in this laboratory a melting range from 6° to 16° C has been reported<sup>1</sup> for crystallization temperatures near 0° C. Van Rossem and Lotichius<sup>2</sup> found that crystals formed at -10° C melted between 2° and 14° C. Both these sets of observations are included in Figure 1.

The results here presented undoubtedly explain many previously reported discrepancies in the temperatures of melting of crystalline rubber. They may also be expected to furnish an explanation of certain effects with stretched rubber recently observed by Treloar<sup>3</sup>, who, lacking the present data, felt that he was not justified in making the assumption that "the melting point of the crystals could depend on the temperature at which they are formed."

There seems to be no reason why the effect discussed here should be limited to rubber and, if investigations are made, this effect may be found in many other organic compounds of high molecular weight.

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# HYSTERESIS IN THE CRYSTALLIZATION OF STRETCHED VULCANIZED RUBBER

## II. X-RAY STUDIES OF THE EFFECTS OF SULFUR CONTENT AND METHOD OF CURING \*

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### INTRODUCTION

Crystallization on stretching has been studied for a large number of compounds under various conditions by Field<sup>1</sup>. That hysteresis in the crystallization process occurs on relaxing the sample was clearly demonstrated in the first paper<sup>2</sup> of this series. The purpose of the present study has been to investigate the entire hysteresis loop for a series of compounds containing sulfur up to eight

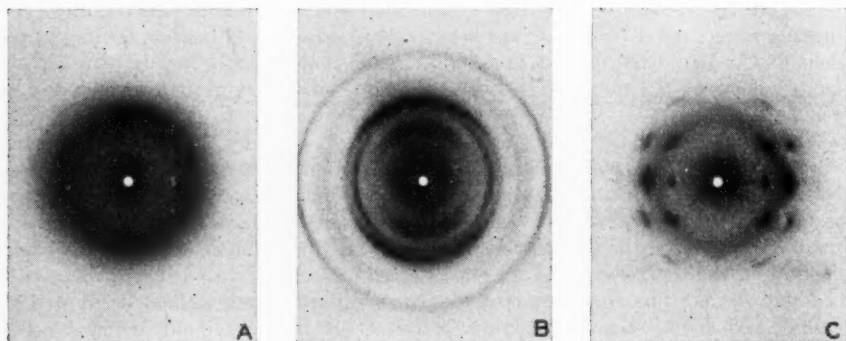


Fig. 1.

per cent, and to investigate the effects on it of time and temperature of curing. Apparently the retraction curve is particularly sensitive to the variables mentioned.

Figure 1 consists of three parts. A shows an ordinary rubber halo derived from a sample of unstretched, dried down, normal latex. If, on stretching a rubber sample, randomly-distributed ordered regions were pulled into line, one would expect to get a typical fiber pattern as shown in B. Finally, after the material was almost completely oriented, one would expect to have the arcs shorten up into sharp spots as in C, which is a typical pattern of stretched raw rubber. But this is not what happens when a rubber sample is stretched. The fiber pattern shown in B does not appear. The transition from the halo as the rubber is stretched is to sharp spots. When the spots first begin to appear, they are as sharp as they ever will be. Their definition does not change with further

\* Paper presented before the Division of Rubber Chemistry of the American Chemical Society at the meeting at St. Louis, Missouri, Apr. 10-11, 1941.

stretching, but they do become more intense. The picture of what really happens then is this: At a given stress on the rubber sample, crystallites, oriented along the axis of stretching, begin to precipitate out of the rubber matrix. As more stress is applied, more crystals are formed. The density of the diffraction spots increases and the density of the halo decreases. The greatest observed degree of crystallization on stretching corresponds to about 80 per cent. Frozen rubber may be 100 per cent crystalline. The degree of crystallization of any sample may be known then by measuring the density of the diffraction spots and comparing this density to some standard.

#### EXPERIMENTAL PROCEDURE

The source of radiation was a Philips Metalix copper-target tube mounted in a Hayes multiple diffraction unit. The tube was operated at 28 K. V. and 20 ma.

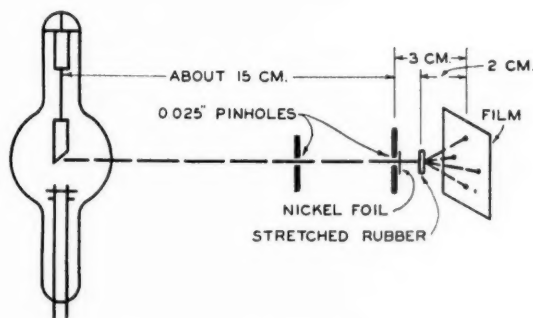


FIG. 2.—Arrangement of apparatus and sample for x-ray analysis.

The setup reported in the previous article is shown in Figure 2. It required an exposure time of one hour. An improved technique has been developed, by means of which good pictures may be taken in five minutes. The sample film distance has been cut to fourteen millimeters, and the nickel film distance to twenty-eight millimeters. A 0.010 inch pinhole is used instead of 0.025 inch. A lead shutter installed over the pinhole is used to start and stop the exposure. One-half the film is shielded during each exposure, so that two pictures may be recorded on a sheet of  $3\frac{1}{4} \times 4$  in. Agfa non-screen x-ray film. The nickel foil placed over the pinhole registers a nickel diffraction ring on the film, which serves as a standard for variations in exposure and developing conditions, and performs at the same time its usual function as a filter for Cu radiation. Each set of films comprising one series is developed at one time. All samples tested were in the shape of standard dumbbell test specimens.

A number of pictures taken by this new method are shown in Figure 3. The second part of the first picture shows crystallization just beginning. The second group shows a high degree of crystallization.

A new Leeds and Northrup recording microphotometer was used to measure the densities of the various portions of the films. Sample microphotometer tracings are shown in Figure 4. The recording paper was ruled with a logarithmic scale. The less intense of the two diffraction spots along the equator is the only one for which a suitable background may be drawn in, and was used in all the measurements given.

A sample set of data is shown in Table I. It is noted that the time interval between the change in elongation and the start of the new picture is about nine

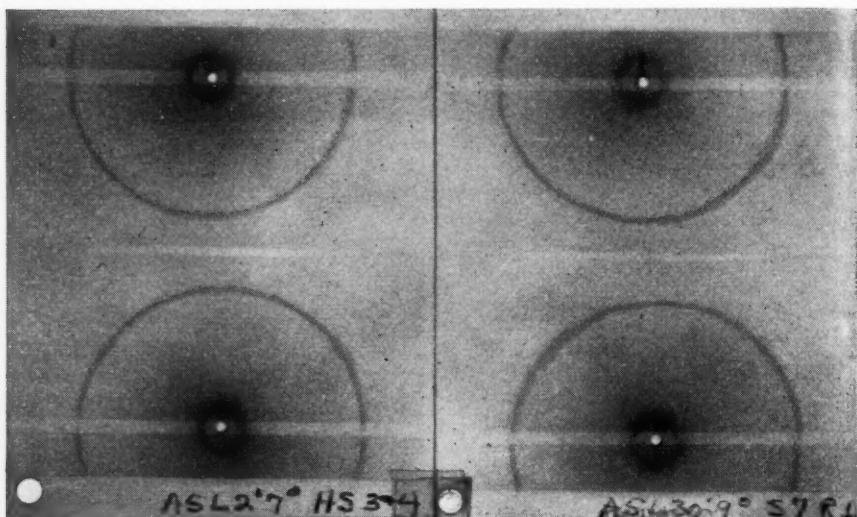


FIG. 3

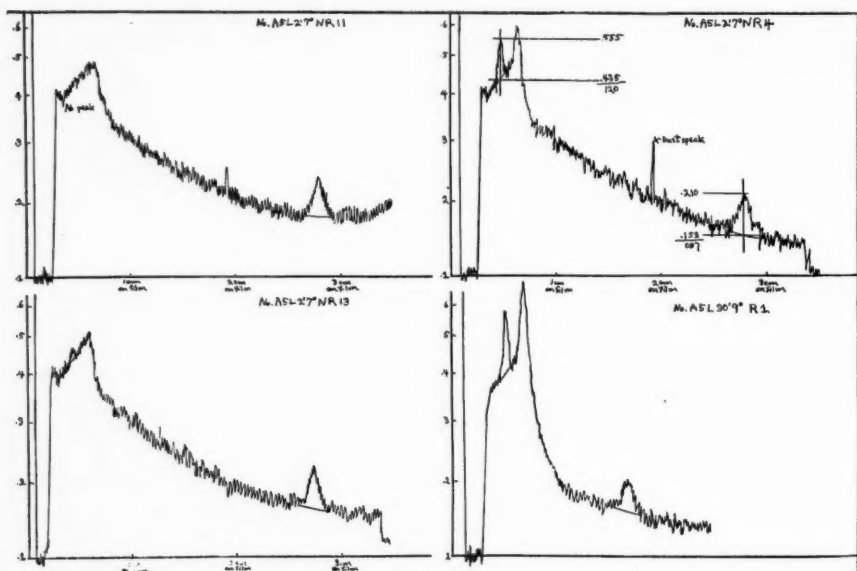


FIG. 4.

minutes. Except in cases where under- or overexposure is definitely known, as indicated in the column labeled "remarks", the average value for the density of the nickel interference is used as the divisor in finding the rubber-spot to

nickel-ring densities ratios. The density of the nickel rings and rubber spots may be measured to  $\pm 0.005$  units, and it is felt certain that the error in the ratios is not greater than  $\pm 0.1$  unit.

March 17  
ASL 60' 239° F.  
5th cycle

TABLE I  
TYPICAL SET OF DATA

	Approximate (percentage)	Elongation (cm.)	Actual length (cm.)	Time (p.m.)	Temperature (° C)	Remarks	Actual elongation (percentage)	Densities		Ratio
								Spot	Ni	
S1	300	8	8	4:30	24.0	—	300	—	—	—
S2	350	9	9	4:45	24.0	½ min. over xpd	350	—	—	—
S3	400	10	10.5	5:00	24.0	—	425	0.062	0.046	1.1 <sub>3</sub>
S4	450	11	11.2	5:15	24.0	—	460	0.094	0.050	1.7 <sub>1</sub>
S5	500	12	12.0	5:30	24.0	—	500	0.110	0.050	2.0 <sub>0</sub>
S6	550	13	13.0	5:45	23.6	—	550	0.138	0.055	2.5 <sub>1</sub>
S7	600	14	14.0	6:00	24.0	—	600	0.182	0.055	3.3 <sub>1</sub>
FOUR-HOUR INTERVAL										
R1	600	14	14.0	10:00	24.6	—	600	0.190	0.055	3.5 <sub>4</sub>
R2	550	13	13.0	10:15	24.6	—	550	0.172	0.055	3.1 <sub>3</sub>
R3	500	12	12.0	10:30	24.6	—	500	0.156	0.055	2.8 <sub>1</sub>
R4	450	11	11.0	10:45	24.6	—	450	0.129	0.055	2.3 <sub>5</sub>
R5	400	10	10.0	11:00	24.6	—	400	0.107	0.055	1.9 <sub>3</sub>
R6	350	9	8.9	11:15	24.6	—	345	0.092	0.063	1.6 <sub>3</sub>
R7	300	8	7.9	11:30	24.6	—	295	0.065	0.060	1.2 <sub>2</sub>
R8	250	7	6.8	11:45	24.6	10 sec. over xpd	240	—	Av. 0.055	
R9	200	6	6.0	12:00	24.6	—	200	—		

## RESULTS AND DISCUSSION

The following experiments were performed on rubber compounds of the following basic composition:

Smoked sheet .....	100
Zinc oxide .....	3
Stearic acid .....	0.5
Zimate .....	0.5

The stock (a) represented in Figure 5 contains, in addition, 2 per cent of sulfur. It was cured for 2 minutes at 307° F, and represented the best cure at this temperature. There is much more hysteresis at 20° C than at 30° C. The retraction curve is quite sensitive to change in temperature. It is necessary to bear this fact in mind in our further discussions.

The compound in Figure 6 had the same composition as that in Figure 5. Figure 6 represents a range of cures at 239° F. In order they are under-<sup>(b)</sup>, best<sup>(c)</sup>, and overcured<sup>(d)</sup>. The hysteresis effect seems to decrease with increasing time of cure. This is all the more evident when it is known that determinations on the 10-minute cure were made at 28-30° C, the 30-minute cure at 21-23° C, and the 60-minute cure at 24-25° C. A similar set of curves was run for a range of cures at 274° F, and the same general effect was noted. There is some evidence (not presented here) that there is less hysteresis for equivalent cures at lower temperatures than at higher temperatures.



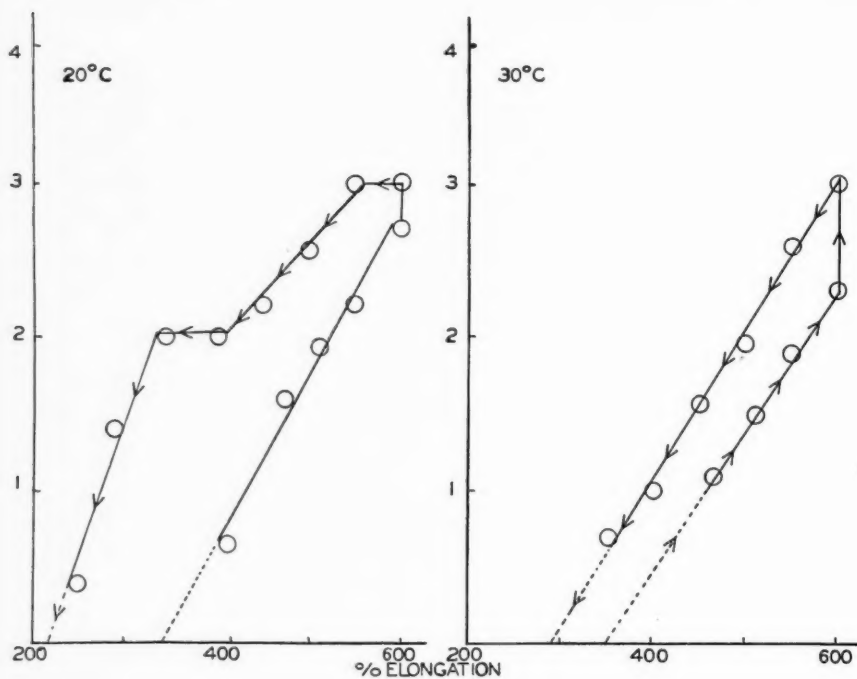


Fig. 5.

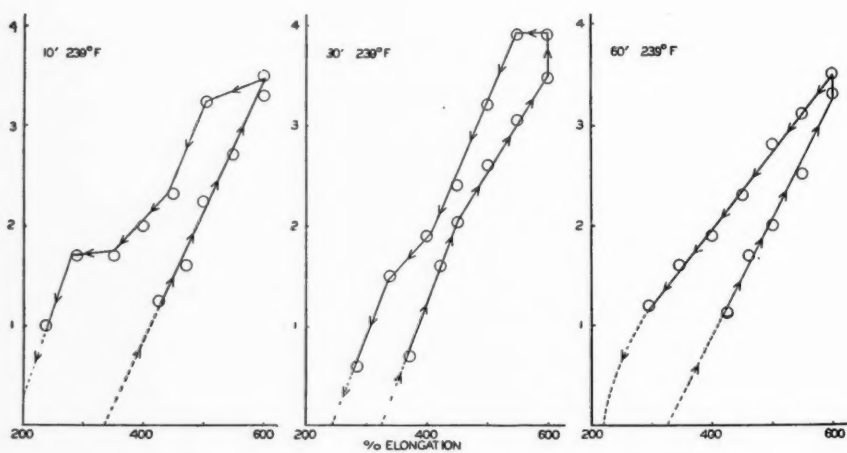


Fig. 6.



Figure 7 shows the effect of varying amounts of sulfur on the hysteresis. The stock represented by A<sup>(e)</sup> contains 1.0 per cent of sulfur; by B<sup>(a)</sup>, 2 per cent of sulfur; C<sup>(t)</sup>, 3 per cent of sulfur; and by D<sup>(g)</sup>, 8 per cent of sulfur. A, C and D were all cured for 60 minutes at 274° F. A sample<sup>(h)</sup>, cured in the same manner and containing only 0.1 per cent of sulfur, did not give any diffraction spots when stretched to 500 per cent elongation. Sample B was cured only 2 minutes at 307° F. It would be expected to give a slightly lower curve if it were cured for a length of time equivalent to the other samples, but its relative position would probably be the same. This indicates that a definite proportion of sulfur would give a stock with the greatest amount of crystallization. This value is somewhere between 1 and 3 per cent sulfur for this given stock.

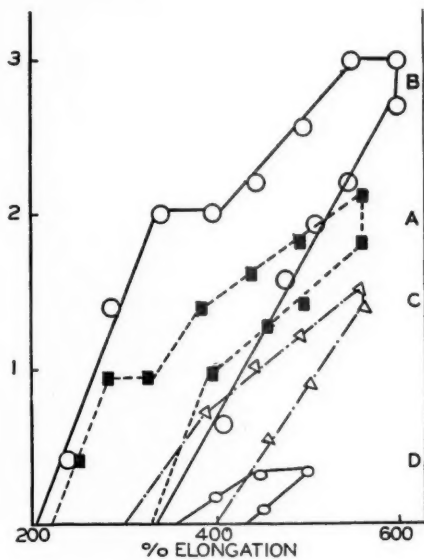


FIG. 7.

All of the curves presented to date have been drawn with broken lines, because the data would not permit smooth curves to be drawn. This was especially true of the retraction curves on samples showing large amounts of hysteresis. A clue to the reason for this was discovered when visible inhomogeneities in retraction were observed in the sample<sup>(t)</sup> shown in Figure 8. Such inhomogeneities were immediately sought in other samples, even where not clearly visible to the eye. The x-ray diffraction method was found very sensitive to the amount of crystalline material present. Figure 9 shows the details in the retraction curves for two different rubber stocks A<sup>(a)</sup> and B<sup>(e)</sup> with large amounts of hysteresis. At the tails of the retraction curves, large inhomogeneities are noted.

Table II shows the evidences for inhomogeneities on stretching. Their magnitudes are not so great as those which are exaggerated by hysteresis in the retraction curves; nevertheless they are much larger than the experimental errors. These inhomogeneities do not show to such a great extent in samples with slight amounts of hysteresis. They do not seem to show to such a great extent

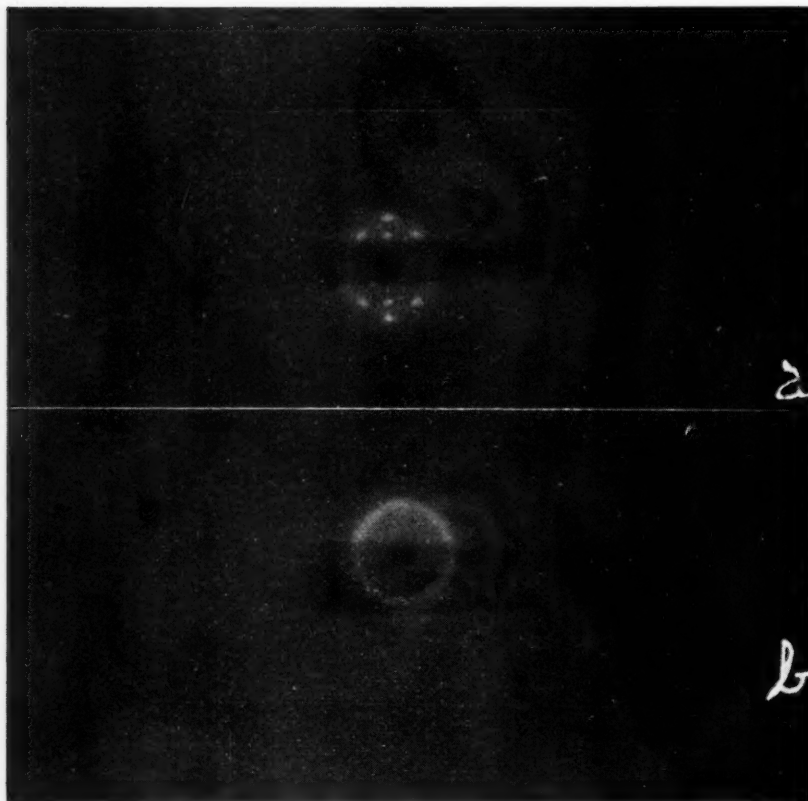


FIG. 8.

TABLE II

## TABLE OF INHOMOGENEITIES ON STRETCHING

Sample No. A5L 10' 274°

	Elongation (per cent)	Time	Temp. (° C)	Spot	Ni	Ratio
TS1 .....	370	12:15	29.0	0.040	0.045	0.9
TS2 .....	370	12:21	29.0	0.035	0.043	0.8
TS3 .....	370	12:30	29.0	0.055	0.043	1.3
TS4 .....	370	12:36	29.0	0.035	0.048	0.7
TS5 .....	370	12:44	29.0	0.050	0.047	1.1
TS6 .....	370	12:51	29.0	None	—	—

Each of the above pictures was taken through a different portion of the sample at the same elongation.

in stocks containing fillers, which apparently help to equalize the system. These hysteresis effects are averaged into all the stress-strain data ordinarily determined for rubber stocks. Indeed, in most cases, it is only by the x-ray method that they may be seen at all.

Confirmation of the existence of these inhomogeneities in stretched rubber is much to be desired. Certainly such a phenomenon would necessarily have to be considered in any efforts to explain the physical behavior of this important material.

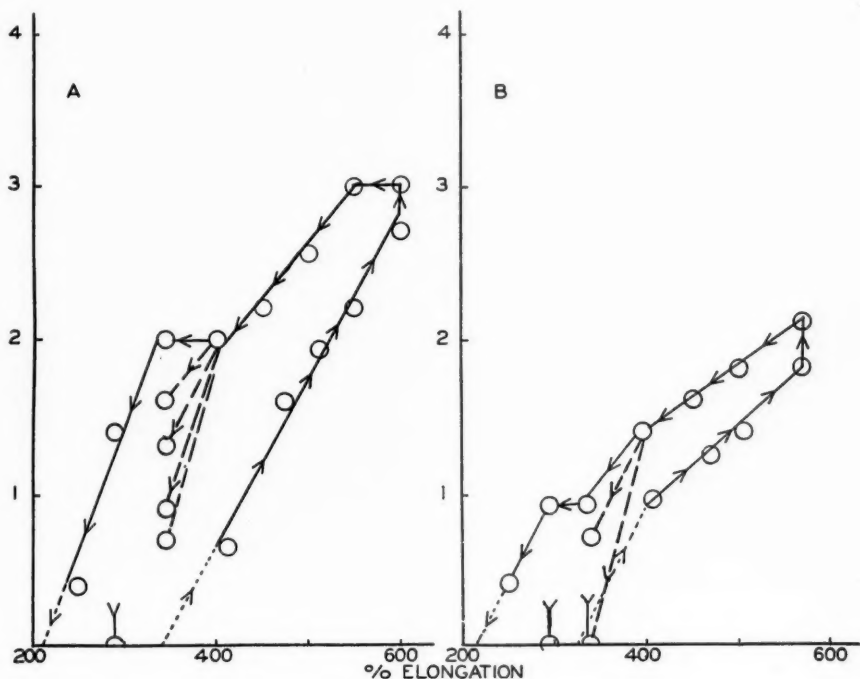


FIG. 9.

## SUMMARY

1. Improvements in technique make possible complete rubber patterns in only five minutes' exposure.
2. The extreme sensitivity of hysteresis in crystallization to changes in temperature at which the stock is investigated is demonstrated.
3. Hysteresis decreases with the time of cure for a given compound.
4. Crystallinity at a given elongation seems to decrease with increasing temperature of curing for equivalent cures over the range of 239-307° F.
5. For the stock studied, at a given time and temperature of cure, the proportion of sulfur giving the greatest crystallinity at 550 per cent is between one and three per cent.
6. Inhomogeneities in the disappearance of crystallinity have been clearly demonstrated, and shown to be an exaggerated localized hysteresis effect.

## APPENDIX

## PHYSICAL TESTING DATA ON RUBBER STOCKS \* REFERRED TO

Stock No.	Stress at 500 per cent elongation (lbs. per sq. in.)	Tensile strength at break (lbs. per sq. in.)	Elongation at break (percentage)	Free sulfur (percentage)	T-50 value ( $^{\circ}$ C)
a. ....	480	3670	820	—	— 6.2
b. ....	255	2470	850	—	+ 7.5
c. ....	585	3900	765	—	— 8.3
d. ....	560	3900	795	—	—17.9
e. ....	215	2070	880	0.011	—
f. ....	505	3720	790	0.026	—
g. ....	1250	3020	660	1.525	—
h. ....	43	275	1180	0.021	—
† i. ....	480	2730	735	—	—

\* All stocks were prepared and tested at the R. T. Vanderbilt Laboratories, and sent to the University of Illinois for x-ray examination.

† Composition of stock i. Smoked Sheet, 100; stearic acid, 1; zinc oxide, 3; tetramethylthiuram disulfide 3.

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# AN X-RAY STUDY OF THE PROPORTION OF CRYSTALLINE AND AMORPHOUS COMPONENTS IN STRETCHED RUBBER \*

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## INTRODUCTION

Under ordinary circumstances, the x-ray diffraction pattern of rubber is similar to that of a liquid displaying an amorphous structure<sup>1</sup>. However, under limited conditions of stretching<sup>2-4</sup> or freezing<sup>5, 6</sup>, rubber exhibits a crystalline phase of its structure in that the x-ray diagram indicates the appearance of crystallites which, in the case of stretching, are aligned along the axis of stretch. Typical diffraction patterns for unstretched and stretched rubber are shown in Figures 1 and 2. Although the mechanism of this transition is not yet fully understood, it resembles in many respects the crystallization of a supercooled liquid<sup>7</sup>. In the early investigations of Katz<sup>4</sup> and of Hauser and Mark<sup>8</sup>, it was learned that the fiber diagram made its appearance only after a minimum elongation had been reached and, as stretching proceeded, the intensity of the diffraction spots increased and the intensity of the halo decreased. The elongation at which the spots attain an appreciable intensity is usually in the range of 150 to 275 per cent, depending largely on the sample, the conditions of stretching and the temperature. The x-ray diffraction phenomena for rubber have been covered in a recent review article, which includes a bibliography on the subject<sup>9</sup>.

Even in highly stretched rubber a faint halo persists, indicating the presence of some amorphous material. Meyer and Mark<sup>10</sup> estimated that at least 80 per cent of very highly stretched rubber is crystalline. The formation of crystallites is very noticeably influenced by the temperature. Thiessen and Wittstadt<sup>11, 12</sup> have shown that an equilibrium condition is attained for crystallization, depending on the elongation, temperature and pressure. According to the fusion curve of Susich<sup>13</sup>, for stretched raw rubber, only amorphous x-ray diagrams appear above a temperature of 90° C.

It is reasonable to expect that the physical properties of rubber will be influenced to a large extent by the coexistence of amorphous and crystalline hydrocarbon in various proportions. Experiments with unvulcanized rubber have already shown this. Thus, Hintenberger and Neumann<sup>14</sup> found that in the case of raw rubber a maximum elongation appeared at relatively small stresses when the elongations were plotted as a function of the constant loads applied over a fixed period of time. Also, a critical range of loadings was found, within which the probability of rupture of the rubber samples was greatest. This maximum became more pronounced with increase in temperature, and its occurrence was explained as a combined effect of flow and crystallization, the latter beginning to occur in this critical region. Later, Hauk and Neumann<sup>15</sup> extended the investigation to vulcanized compounds, with similar results. Braun<sup>16</sup> found that samples of stretched

\* Reprinted from the *Journal of Applied Physics*, Vol. 12, No. 1, pages 23-24, January 1941.

vulcanized rubber tended to fail at intermediate elongations when stretched for a long period of time. A maximum dynamic fatigue life at relatively low stresses also has been demonstrated<sup>17</sup>.

The effect of vulcanization on the x-ray diagram was investigated by Katz and Bing<sup>18</sup>. Using a much higher sulfur content than is required in modern compounding, they found that higher elongations were necessary for the appearance of the fiber diagram as vulcanization progressed. Since milled raw rubber does

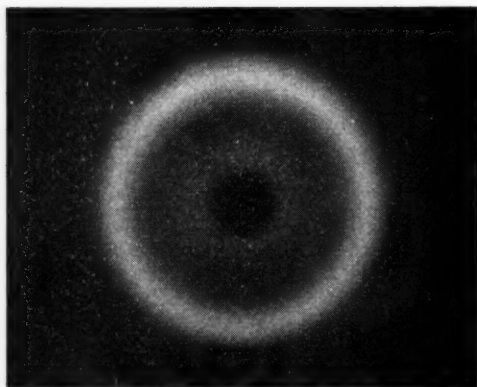


FIG. 1.—Unstretched rubber.

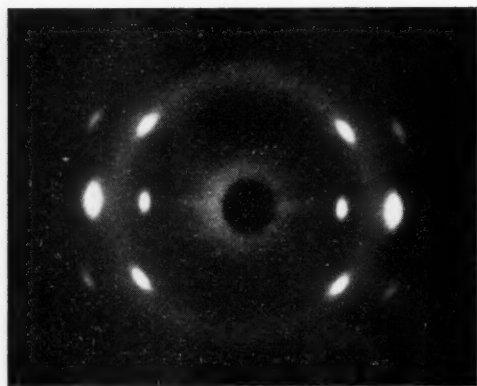


FIG. 2.—Stretched rubber.

not give a fiber diagram under normal conditions, it is reasonable to believe that vulcanization assists crystallization by means of molecular immobilization until the rigidity introduced by the network of primary valence cross-linkages begins to prevent the movement of the molecules into the crystal lattice<sup>9</sup>.

The basis of modern rubber technology lies in the ability to vulcanize rubber with a wide range of physical properties, thus making possible its adaptation for any particular condition of service. This result is secured by the use of an extensive array of compounding ingredients, including pigments, softeners, etc., but more particularly by the selection of suitable accelerators or chemical agents which

promote vulcanization. This work was concerned with measurements of the relative proportion of crystalline and amorphous material in typical stretched vulcanizates in an effort to find some connection here with the physical properties.

### EXPERIMENTAL PROCEDURE

A General Electric x-ray diffraction unit, equipped with a Kenotron rectifier and General Electric copper anode tube, was used to obtain the diffraction patterns. The tube was operated at 35 kv. potential and 25 ma. For the majority of the patterns, the  $\text{CuK}\beta$  radiation was filtered out by means of a nickel foil. A nonrecording microphotometer was used to measure photographic densities.

To carry out experiments on stretched rubber above room temperature, an especially designed thermostat was used. This consisted of a jacketed copper block around which oil was circulated by means of a gear pump. The oil was maintained at a constant temperature by flowing through a copper spiral immersed in a

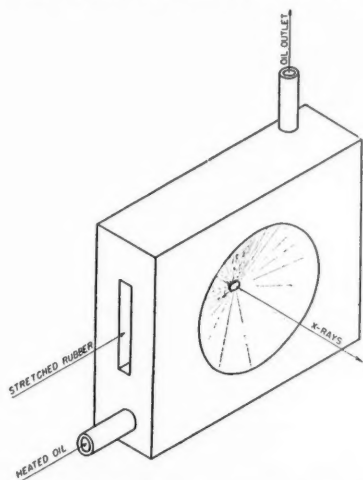


FIG. 3.—Sketch of thermostat.

constant temperature bath. The temperature of the sample was measured by means of a thermocouple. To permit the passage of the x-ray beam, the block was provided with windows which were covered with Cellophane. A sketch of the arrangement is shown in Figure 3.

It is known that the intensity of the diffraction for vulcanized rubber depends to some extent on the stretching procedure, and, in fact, a hysteresis effect for crystallization has been demonstrated by Iguchi and Schossberger<sup>19</sup> and by Clark<sup>20</sup>. In this work, a standard procedure for stretching was adopted. Strips of vulcanized rubber were cut from 2-mm.-gauge test sheets by means of a die. These were stretched in a uniform manner by means of a falling weight, the desired elongation being obtained on the initial stretch by adjusting the distance through which the weight fell. The same procedure was used for stretching strips of raw rubber which were cut from uniform sheets of evaporated latex. Several gauges of the latter were used to determine the effect on the measured crystallinity. A micrometer dial gauge was used to determine the thickness of the rubber samples.

It has been pointed out that the amorphous and crystalline phases of stretched



rubber exist simultaneously and, as stretching proceeds, the intensity of the diffraction spots increase while the intensity of the halo decreases. This relationship offers a possibility of calculating the relative amount of crystallinity in stretched rubber by matching the intensity of the halo with that produced by an unstretched sample of reduced thickness. To make this calculation, the intensity of the halo as a function of the thickness of the unstretched rubber must be known. This is shown in Figure 4. The conditions of exposure and development for these patterns were carefully controlled and corrections were made for any variation in tube output by means of a control spot from the incident beam which was simultaneously exposed on the film through a thin lead strip. The operation of the tube was so steady that, with ordinary precautions in exposure and development, patterns were obtained which required at most only small corrections, as ascertained by variations in the density of the control spot. It is realized that the radiation producing the control spots was harder than the  $\text{CuK}\alpha$  radiation producing the

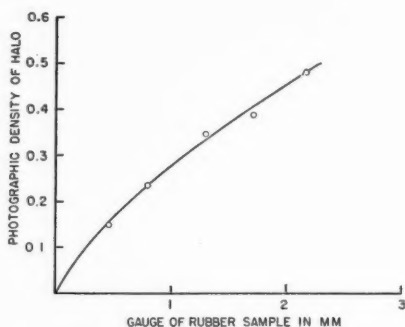


Fig. 4.—Halo intensity for unstretched, unvulcanized rubber.

pattern because of the filtering action of the lead, but this effect was minimized because any corrections based on the control spots were so small.

The proportion of crystalline material at any given elongation may be calculated by referring to the relationship shown in Figure 4. Because of crystallization resulting from stretching, the intensity of the halo for a stretched sample is less than that for an unstretched sample of the same thickness. From the measured intensity of the halo for a stretched sample, it is possible to obtain from Figure 4 the effective thickness of the amorphous material remaining in the sample, and the difference between this and the actual gauge represents the amount of crystallized material. Thus, if  $X_0$  is the measured gauge of a stretched rubber sample at any given elongation and  $X$  is the effective thickness of amorphous material, the percentage of crystalline material may be calculated by means of the formula:

$$\text{Per cent crystalline material} = \frac{100(X_0 - X)}{X_0}.$$

It should be noted that only the intensity of the halo was considered in the derivation of the above formula, the diffraction spots receiving no consideration.

Since the crystalline material is formed on stretching at the expense of the amorphous phase, it is evident that the ratio of the intensity of the  $A_1$  diffraction spot to the intensity of the halo is a measure of the crystallinity. This has the

advantage of being independent of all exposure factors. The relation between this ratio and the percentage crystallinity, shown in Figure 5, was obtained from measurements of patterns which were carefully controlled in the manner previously described, together with application of the above formula to these same patterns. Once this relation is carefully established, the percentage crystallinity may be readily obtained for a given spot-halo ratio, regardless of exposure conditions. This calibration curve, so to speak, was applied to the vulcanized gum stocks used in this work to determine the crystallinity under various conditions.

On all the films for vulcanized rubber, the quantities measured were the densities of the  $A_1$  spot and the halo. A uniform procedure was followed in obtaining halo densities. Density values were secured across a diameter of the halo. These were plotted, a back-ground density was determined from this curve, and the maximum density above this was taken as the density of the halo.

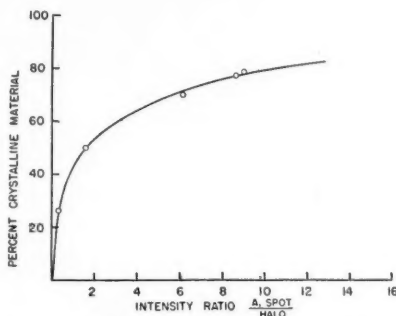


Fig. 5.—Compositions indicated by intensity ratios in the patterns.

## EXPERIMENTAL RESULTS

### CRYSTALLINITY OF STRETCHED RAW RUBBER

x-Ray diffraction patterns were recorded for samples of evaporated latex sheets at elongations ranging from 250 to 700 per cent under two different conditions. In the one case, the gauge of the sample was 2 mm. before stretching, the final gauge therefore varying according to the degree of stretch. In the other case, the initial gauge was so adjusted that the gauge after stretching was always 0.25 mm. The relative proportions of crystalline and amorphous material present, when samples were stretched according to the above conditions, is comparable as shown in Figure 6, so that in the work which follows, the experimental procedure was simplified by using samples of the same initial gauge. These curves, by extrapolation, indicate that the crystallization has advanced far enough to become evident in the neighborhood of 175 per cent elongation. At the start, the curves are practically linear, but approach asymptotically a value of about 80 per cent at the higher elongations. This implies that the maximum amount of crystalline material created by stretching is about 80 per cent of the total rubber. It is probable that the crystalline proportion would be slightly greater than this if consideration were given to the impurities in the latex which tend to increase the intensity of the halo. It would be difficult to check this result with crystallization because of freezing because, in the latter case, Debye-Scherrer rings appear in the region of the halo, making intensity measurements of the halo too unreliable.

Taking accepted values of 0.92 and 0.95 for the densities of amorphous and highly stretched rubber, respectively, a density of 0.965 for crystalline rubber is deduced. This compares well with the highest measured value of the density obtained from rubber that had been stretched and frozen.

The crystallinity at various elongations of evaporated latex sheet was determined from x-ray diffraction patterns recorded at room temperature. Diagrams for these same samples were obtained at 90° C and again at room temperature at the same constant elongation, and the effect on the crystallinity was observed. These changes in crystallinity are shown in Figure 7. The courses of the crystalli-

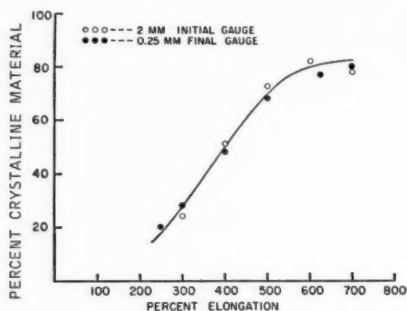


Fig. 6.—Crystallization of stretched, unvulcanized rubber.

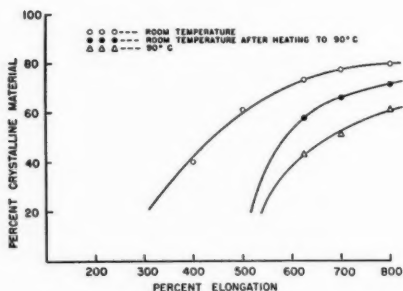


Fig. 7.—Effect of temperature on the crystallinity of unvulcanized rubber.

zation curves in the lower range were determined from the maximum elongations at which crystallization had not yet become evident.

According to one point of view<sup>11</sup> there is a statistical distribution of melting points over a temperature range, so that the decrease in crystallinity at the higher temperature would be attributed to the disappearance of crystallites whose melting points are 90° C or less. On the other hand, we may be dealing with a system which reaches an equilibrium analogous to that reached by a saturated solution in contact with the solid solute. Another factor to be considered in the lower amount of crystallinity at the higher temperature is plastic flow. This accounts for the failure of the crystallinity to regain its original value at room temperature after the heating for 15 minutes at 90° C and re-exposure without retraction. The amount of plastic flow undoubtedly increases with the time of heating, making this effect more pronounced the longer the time of heating. Also,

plastic flow is reduced by the increased amount of crystallinity at higher elongations. At lower elongations, after the heating, plastic flow is sufficient to prevent any recrystallization of the clamped sample at room temperature. This is accompanied by a higher permanent set at lower elongations.

## CRYSTALLINITY IN STRETCHED VULCANIZED RUBBER

The formation of crystallites in vulcanized rubber is influenced to a very large extent by changes in internal structure brought about by processing, by the action of compounding ingredients and by the curing treatment. Since the greatest differences in crystallinity would be expected to be found between vulcanizates having a wide range of physical properties, x-ray diffraction patterns of the gum stocks shown in Table I were investigated under various conditions. The trade names

TABLE I

Compound	A	B	C	D
Smoked sheet .....	100	100	100	100
Zinc oxide .....	1	2	1	3
Sulfur .....	3	2	2	5
Stearic acid .....	0.5	—	—	—
Captax .....	0.5	—	—	—
P.P.D. ....	—	2	—	—
Zimate .....	—	—	1	—
D.P.G. ....	—	—	—	1

of the accelerators used in compounding these stocks are listed below with their respective chemical names.

Captax .....	2-Mercaptobenzothiazole
Accelerator 552 (P.P.D.) .....	Piperidinium pentamethylenedithiocarbamate
Zimate .....	Zinc dimethyldithiocarbamate
D.P.G. ....	Diphenylguanidine

Hereafter, Accelerator 552 will be referred to as P.P.D. throughout this work. The range of physical properties for these vulcanizates is shown in Table II.

TABLE II

Compound	Cure		Stress at 500 per cent elongation kg. per sq. cm.	Tensile kg. per sq. cm.	Ultimate elongation (per cent)
	Min.	Temp. F°			
A .....	30	260	18	126	815
B .....	10	260	70	244	675
C .....	20	260	28	166	770
D .....	15	285	29	160	765

The effect of the time of cure on the crystallinity in compounds A and D is shown in Figure 8. As curing progresses, the crystallinity increases sharply to a maximum and then gradually decreases. The position of this maximum undoubtedly changes relative to the curing time for different compounds, as indicated by the curves for the two compounds shown here. In the early stages of the vulcanizing process, no crystallization on stretching is apparent. However, crystallites are very readily formed when the uncured stock is frozen, as is

evidenced by the appearance of the Debye-Scherrer rings in the x-ray pattern. This is understandable if it is considered that, extending throughout the structure of the rubber, there are more or less ordered regions which might be compared with the molecular clusters throughout a liquid which give rise to the halo in the diffraction pattern. These ordered regions become the nuclear centers from which crystallization proceeds when internal forces are set up by stretching or freezing. The extensive milling and processing in preparation for vulcanization apparently do not completely destroy these ordered regions, but they do increase the plasticity to the extent that the internal forces set up by stretching are insufficient to improve the lattice spacing in these regions to form crystallites. When vulcanization has reached the point where the network of primary valence cross-linkages noticeably reduce the plasticity, the internal stresses produced by stretching become effective in crystallite formation. This step demonstrates that vulcanization actually assists in the crystallization process. Once crystallization has started,

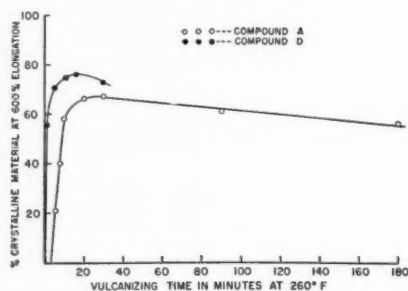


Fig. 8.—Dependence of crystallinity on cure.

anchorage are formed for adjacent portions of amorphous material, thus discouraging plastic flow and creating new points of stress for further crystallization. It is conceivable that, in the early states of vulcanization, such secondary bonds are more effective than the cross-linkages of the network. As vulcanization advances, there exist simultaneously the forces of crystallization and of increasing numbers of cross-linkages until an equilibrium between these two is reached and the optimum condition for crystallization is attained, as shown by the maximum crystallinity appearing in the curve of Figure 8. With additional cure, the complexity of the network increases and interferes more and more with the molecular mobility, thus reducing the possibility of forming crystallites. This is represented by that portion of the curve appearing to the right of the maximum.

The tensile strength of vulcanized rubber depends on the extent of the vulcanization and, in considering a range of curing times, a peak or maximum tensile strength is reached, as shown in Figure 9. The cure producing a vulcanizate having the most desirable properties for a given purpose is considered as the "best cure". For this particular compound, (A), for general purposes, the "best cure", on the basis of practical experience, is judged to be the curing time that produces a vulcanizate whose tensile strength is about 10 per cent less than the peak. On this basis, the 30-minute cure may be classified as the best cure. It is interesting to note that for this compound the most favorable condition for crystallite formation coincides approximately with the time for best cure.

The relationship between the crystallinity and the elongation, as it is effected by the curing time for vulcanizates B and C, is shown in Figures 10 and 11,

respectively. Crystallization decreases with increasing curing times for these compounds. Obviously, the lowest cures for these compounds, according to Figure 8, have either just reached the condition for maximum crystallinity or have already exceeded it.

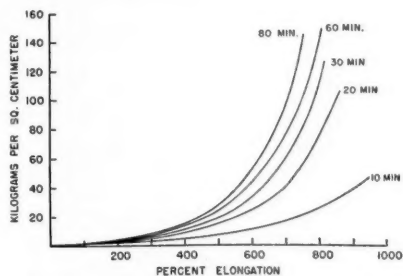


FIG. 9.—Stress-strain curves for compound A.

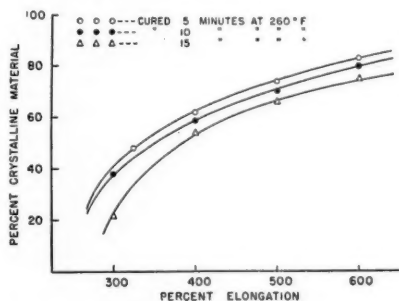


FIG. 10.—Proportion of crystalline rubber in compound B.

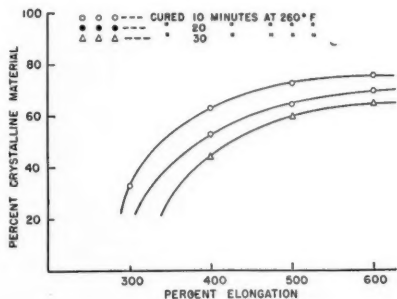


FIG. 11.—Proportion of crystalline rubber in compound C.

Different accelerators should have considerable effect on the crystallization of stretched vulcanized samples into which they have been incorporated, on account of the various degrees of complexity and the type of network induced by their presence. The effectiveness of various accelerators on crystallite formation for a series of typical gum stocks at so-called best cure over a range of elongations is shown in Figure 12. The composition of these stocks is shown in Table III.

Physical test data for these vulcanizates are tabulated in Table IV. The relative amount of crystalline material can be readily observed from these curves. At 500 per cent elongation, for example, the P.P.D. vulcanizate *E* possesses the largest amount of crystallinity for the samples investigated. This is followed in order by compounds containing a Captax-D.P.G. mixture, *F*; D.P.G., *G*; Captax,

TABLE III

Compound	Parts by weight							
	<i>E</i>	<i>F</i>	<i>G</i>	<i>H</i>	<i>J</i>	<i>K</i>	<i>L</i>	<i>M</i>
Rubber .....	100	100	100	100	100	100	100	100
Sulfur .....	3	3	3	3	—	3	3	3
Zinc oxide .....	5	5	5	5	—	5	5	—
P.P.D. ....	2	—	—	—	—	—	—	—
Captax .....	—	0.25	—	0.5	—	—	—	—
D.P.G. ....	—	0.25	0.5	—	—	—	—	—
Dinitrobenzene .....	—	—	—	—	10	—	—	—
Calcium oxide .....	—	—	—	—	—	—	10	—
Lead oxide .....	—	—	—	—	10	—	—	—

TABLE IV

Compound	Cure		Stress at 500 per cent elongation kg. per sq. cm.	Tensile kg. per sq. cm.	Ultimate elongation (per cent)
	Min.	Temp. F °			
<i>E</i> .....	5	240	50	230	720
<i>F</i> .....	20	260	33	220	790
<i>G</i> .....	40	285	28	148	760
<i>H</i> .....	40	260	18	136	830
<i>J</i> .....	20	285	18	54	740
<i>K</i> .....	180	285	7	46	935
<i>L</i> .....	80	285	20	97	825
<i>M</i> .....	240	285	6	31	1050

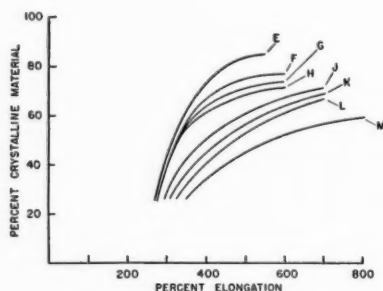


FIG. 12.—Crystallinity of compounds with different accelerators.

*H*; dinitrobenzene, *J*; ZnO, *K*; CaO, *L*; and straight sulfur, *M*. This sequence may be altered to some extent by variation in compounding or curing of stocks utilizing these same accelerators.

From the general appearance of Figure 12, the curves fall into two groups, one with higher amounts of crystallinity for stretched samples containing organic accelerators, and the lower group which includes the inorganic accelerators. Here the crystallinity approaches that in compounds cured with straight sulfur.



The influence of temperature on the formation of crystallites in stretched vulcanized rubber is shown in Figure 13. At the same elongation, the number of crystallites is reduced as the temperature increases. This linear relationship may have some connection with the stress-temperature relation shown by Ornstein, Eymers, and Wouda<sup>21</sup>. The crystallinity before and after heating 15 minutes at 90° C, compared with the amount existing at 90° C, is shown in Figure 14. As

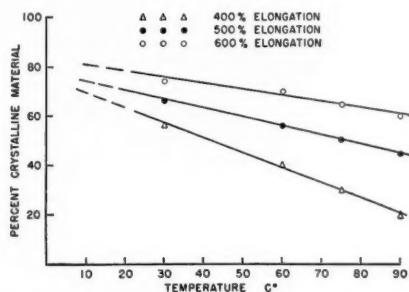


Fig. 13.—Dependence of crystallinity on temperature at constant elongation (compound A).

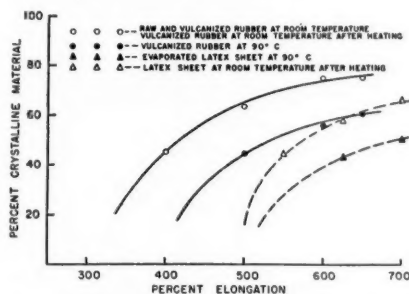


Fig. 14.—Effect of temperature on crystallization.

in the case of raw rubber, these patterns were obtained by reëxposing the same sample without retraction. The reduction in the number of crystallites at the higher temperature may be explained on the same basis as was discussed in the case of raw rubber. Since there was no measurable amount of set, it may be safely assumed that the network introduced by vulcanization has minimized plastic flow; thus no additional decrease in crystallinity would be expected from this source. This probably accounts for the reëstablishment of the original amount of crystallinity at room temperature after heat treatment. The effect of this heating on the cure was negligible. The crystallinity in evaporated latex sheets under the same conditions is also shown in this figure. The original amount of crystallinity at room temperature is practically the same for these raw and vulcanized rubber samples. The greater effect of temperature on the crystallinity for the raw rubber is clearly shown. At the higher elongations, where the crystallinity retards plastic flow in raw rubber, the difference in crystallinity occurring at 90° C, and at room temperature after heating, are about the same as that for vulcanized rubber. This is an indication of the way in which the structure of the raw rubber persists in the vulcanizate. Roughly, the plastic flow appears to be responsible for about one-half the decrease caused by heating in the crystallinity of stretched raw rubber.

## CRYSTALLINITY AND CREEP PHENOMENA

The fundamental differences which may exist in the internal structure of stretched rubber, as previously disclosed, may find a direct correlation in some cases with physical behavior of the compounds. That this should be especially demonstrable in the case of creep phenomena can be surmised from the experiments of Hintenberger and Neumann<sup>14</sup> and of Hauk and Neumann<sup>15</sup>, to which reference has already been made.

When a strip of vulcanized rubber is subjected to a constant load over a considerable period of time, an increase in length over the initial elongation occurs. This phenomenon is often referred to as creep. Such changes in length are attributed to a gradual establishment of equilibrium between the liquid and crystalline phases in rubber, a process into which x-ray diffraction studies should give some insight. Therefore, a more detailed investigation regarding the relation

TABLE V

Compound	Parts by weight	
	N	P
Smoked sheet .....	100	100
Zinc oxide .....	3	3
Sulfur .....	3	3
Stearic acid .....	4	4
Captax .....	1	1
Agerite (phenyl-naphthylamine) .....	1	1
Pine tar .....	3.75	3.75
Gas black .....	—	48

TABLE VI

Compound	Cure		Stress at 500 per cent elongation kg. per sq. cm.	Tensile kg. per sq. cm.	Ultimate elongation (percentage)
	Min.	Temp. F °			
N .....	70	260	46	188	670
P .....	70	260	208	288	610

between the crystallinity and creep in rubber was carried out. It was of particular interest to follow the changes in structure occurring when a stretched sample was allowed to creep through the elongation at which crystallization ordinarily appears.

Samples were prepared by cutting uniform strips, 2 mm. by 4 mm. from similarly compounded vulcanizates, one a gum stock and the other with 48 parts of gas black. The composition of these stocks is shown in Table V.

The physical properties for these vulcanizates are shown in Table VI. These were hung in a cabinet, maintained at a constant temperature of 35° C, and stretched under constant loads by means of weights. For the compound with no black, a series of weights was used giving the following initial elongations: 140 per cent, 185 per cent, 210 per cent, 235 per cent, 280 per cent, 370 per cent, and 510 per cent. Since crystallization ordinarily occurs at about 275 per cent for this vulcanizate, the above range of elongations covers the region above and below the point at which crystallites appear. Thus, the behavior in regard to crystallinity may be investigated as the rubber is permitted to stretch through the transition region in the neighborhood of 275 per cent elongation.

For vulcanizates into which 48 parts of gas black is incorporated, the loads applied produced the following initial elongations: 60 per cent, 75 per cent, 110

per cent, 135 per cent, 170 per cent, 180 per cent, and 215 per cent. For compounds with this quantity of gas black, about 150 per cent elongation is sufficient to make crystallization evident<sup>22</sup>. This range of elongations lends itself to the same studies as the ones used for the compounds with no carbon black loading.

All of these samples were allowed to stand under constant load for about 3½ months, during which interval measurements were made to follow the progress of the creep. The percentage creep was determined by the ratio of the increase in elongation to the initial elongation. When the percentage creep was plotted as a function of the time, typical creep curves were obtained, as shown in Figures 15 and 16. For the low stress of 97 grams per sq. mm., in the case of the gum stock

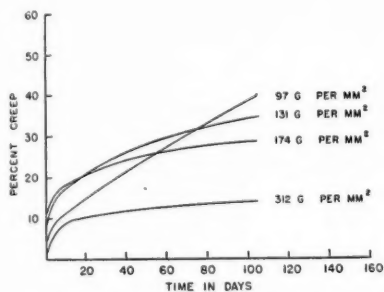


Fig. 15.—Creep curves for vulcanized gum stock (*N*).

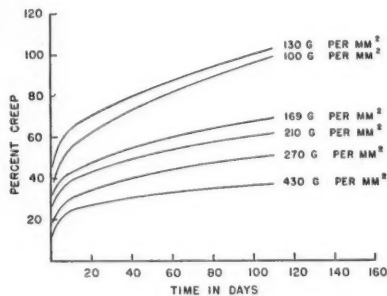


Fig. 16.—Creep curves for vulcanized carbon black stock (*P*).

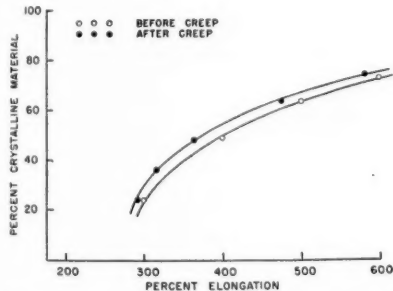


Fig. 17.—Crystallization in gum stock (*N*) before and after creep.

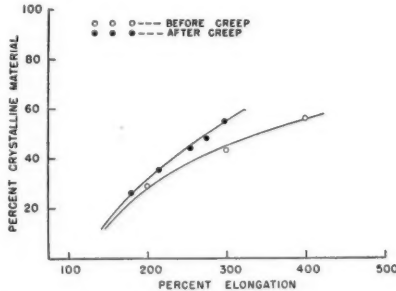


Fig. 18.—Crystallization in carbon black stock (*P*) before and after creep.

*N*, Figure 15, the initial creep is low and the rate of creep is most rapid. For convenience, the stress is expressed here in terms of the cross-sectional area before stretching. As the stress is increased, the initial creep increases, with a corresponding decrease in the rate of creep thereafter. However, as Hauk and Neumann<sup>15</sup> observed, a maximum is reached and, as greater stresses are applied, a smaller initial creep occurs, followed by a low rate of creep. The creep-time relation for the gas black stock *P* behaves in a similar manner, except that a greater amount of creep occurs than for the gum stocks, as shown in Figure 16.

At the end of the 3½-month period, the creep samples were clamped to aluminum strips while still under stress, and x-ray diffraction patterns were recorded. The crystallinity as a function of the final elongation after creep is plotted in Figures 17 and 18. The control curve in each case was obtained from x-ray diffraction data

obtained immediately after stretching. For both the gum and carbon black stocks, the crystallinity is greater for the creep samples. The most obvious explanation for this is that, as equilibrium between the liquid and crystalline phases is becoming slowly established, an opportunity is offered for additional crystallites to form over the number created immediately on stretching. This has been verified to some extent by a stretched vulcanized rubber sample which was permitted to stand for two weeks at constant elongation. At the end of this time a substantial increase over the crystallinity present at the end of one day was noted, confirming observations of Thiessen and Wittstadt<sup>11</sup>.

Other interesting relations between the crystallinity and creep may be shown. One of these may be observed when these two quantities for the gum and carbon black stocks are plotted simultaneously as a function of the elongation, as shown in Figures 19 and 20. In both instances, crystallization becomes evident as the

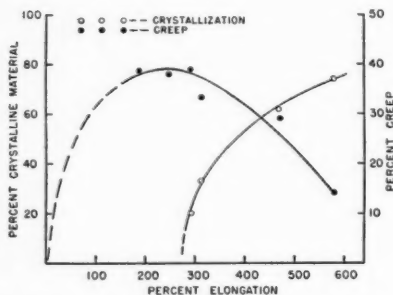


Fig. 19.—Crystallization and creep as functions of the elongation (compound *N*).

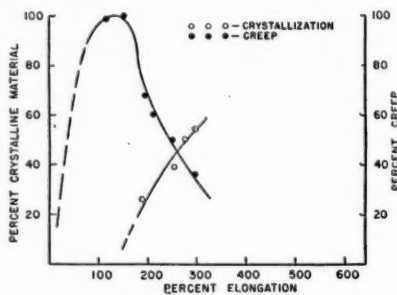


Fig. 20.—Crystallization and creep as functions of the elongation (compound *P*).

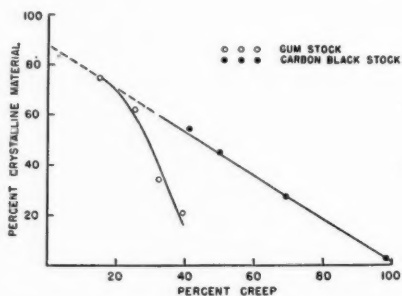


Fig. 21.—Relation between creep and crystallization.

creep reaches its maximum value. As was pointed out earlier, this maximum was explained by Hauk and Neumann<sup>15</sup> as the combined effect of plastic flow and crystallization. The simultaneous relationship shown here is conclusive evidence of the effect of crystallization on the behavior of vulcanized rubber stretched under constant load. This effect is brought out in another way in Figure 21, where the relation between creep and crystallinity is shown. The decrease in creep for the carbon black stock is approximately linear, and coincides with the curve for the gum stock at the higher percentages of crystallinity. If it is assumed that crystallization has reached its maximum extent when no further creep occurs,

then, by extrapolation, the proportion of crystalline material is shown to be about 85 per cent of the total rubber. This is in substantial agreement with the amount previously determined for highly stretched rubber.

The larger creep for the carbon black stock as compared to the gum stock for low percentages of crystalline material, may find an explanation in the relatively poor alignment of the crystallites which exists in the carbon black stock<sup>22</sup>. For this reason, at least, the same degree of crystallinity in the two stocks does not imply the existence of identical internal structures.

#### CRYSTALLINITY AND THE PHYSICAL PROPERTIES OF RUBBER

In the discussion of creep phenomena, it was shown that crystallization contributes an important, if not a major, part in the ability of rubber to withstand the high stresses generally associated with it. Since the physical properties of rubber may be controlled by the type of accelerator used, and the crystallinity has been shown to vary for different accelerators, some relationship between crystallinity and physical characteristics should be available.

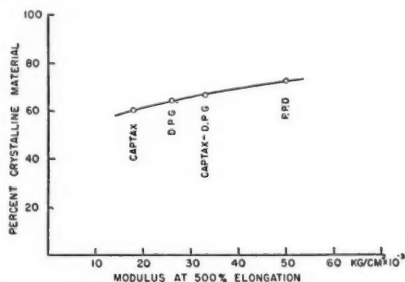


Fig. 22.—Modulus *vs.* crystallinity for different gum stocks.

In testing rubber, a quantity widely used as a measure of the physical properties is the stress required to produce a given elongation. This is spoken of as a modulus. The crystallinity is plotted as a function of the modulus at 500 per cent elongation for gum stocks cured with different accelerators in Figure 22. That crystallinity plays an important role in the strength of rubber when it is stretched is verified, since the vulcanizate with the highest modulus also displays the greatest amount of crystallization. The data were obtained from patterns recorded for the "best cures".

When the crystallinity is compared with the modulus at 500 per cent elongation for a technical range of cures of the same compound, as shown in Figure 23, the modulus increases with cure and the crystallinity decreases. At first glance, these results would seem to be inconsistent with those obtained in connection with Figure 22. However, they are comprehensible if considered in the light of the discussion pertaining to the mechanism of crystallization appearing elsewhere in this work. In the first place, the amount of crystalline material appearing in Figure 22 was obtained from the "best cures", which should be somewhere near the curing time most favorable for crystallite formation. On the other hand, crystallinity decreases with additional vulcanization, due to molecular immobilization, and the modulus indicates that the primary valence cross-linkages are be-

coming very effective in increasing the strength of the rubber. When this occurs, it generally reduces the extensibility of the rubber.

Crystallites in rubber give evidence of the existence of a certain proportion of hydrocarbon in a state which has a definite chemical and physical structure. The amorphous component, on the other hand, is more indefinite. Its exact constitution is probably never identical in different cases, and eludes this x-ray analysis. Nevertheless, measurements of the proportions of these two fundamental components in stretched rubber can, from the foregoing, be judged to give many significant results.

The author wishes to express his indebtedness to S. D. Gehman for his helpful suggestions. M. J. DeFrance and members of the Research Compounding Division kindly furnished the vulcanized compounds used and the standard test data.

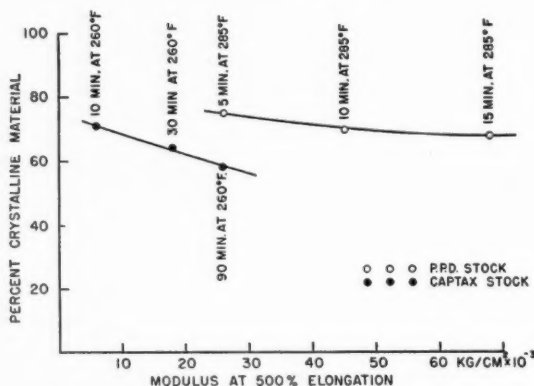


FIG. 23.—Modulus vs. crystallinity for different cures.

### SUMMARY

A method is described for obtaining a quantitative measure of crystalline hydrocarbon present in stretched rubber samples by comparing the intensities of the diffraction spots and the amorphous halo appearing in the x-ray diagrams. This method has been applied to a study of the crystallinity of stretched vulcanized rubber as it is affected by different vulcanization accelerators, variations in extension, temperature, and cure. To illustrate a connection between the physical performance of a rubber vulcanizate and its degree of crystallization, measurements were made of the relation of crystallinity to creep when the rubber was stretched to different initial elongations under constant loads. The creep as a function of the elongation has a maximum value at the same intermediate elongation for which crystallization becomes appreciable. At higher elongations, increased crystallinity results in a diminution of the creep. The ultimate strength and extensibility generally associated with stretched vulcanized rubber is the result of the combined effect of primary valence cross-linkages formed by vulcanization and the formation of crystallites caused by stretching. Crystallization is an important factor in maintaining the relatively high strengths of vulcanizates having a greater range of extensibilities. In general, the physical properties and performance of vulcanized rubber is related to the amount of crystalline material formed on stretching, which depends on the structural characteristics of the vulcanizate.

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# INFRA-RED SPECTRA OF RUBBER AND HIGH POLYMERS \*

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## INTRODUCTION

The rubber industry is interested in all methods for studying the structure of highly polymerized substances. Infra-red spectroscopy has been recognized by recent workers<sup>1, 2</sup> as a possible means for determining the valence forces in long chain molecules. Accordingly, the infra-red spectra of rubber and related compounds have been measured by several workers. An investigation of rubber, gutta percha, indene, polyindene, styrene, polystyrene, polyvinylacetate and polyvinylchloracetate has been carried out by Stair and Coblentz.<sup>3</sup> Later Williams<sup>2</sup> measured natural and vulcanized rubber, rubber hydrochloride, isoprene, styrene and polymerized butadiene in the region between  $2.5\mu$  and  $9\mu$ , but his spectra of rubber did not agree with that of Stair and Coblentz. Williams and Taschek<sup>4</sup> reported that the bands in rubber become broader with increasing stretch. Recently a rough survey of the infra-red transmission of rubber, Pliofilm, Vinylite XYSG, Shawinigan V-15, polystyrene, methyl methacrylate polymer and Cellophane has been made by Wells.<sup>5</sup> The Raman data of rubber obtained by Gehman and Osterhof<sup>6</sup> are in fair agreement with the infra-red results of Stair and Coblentz.

In the absence of a complete theory of the vibrations of chain molecules the interpretations of these spectra have been empirical. Thus a correlation of infra-red and Raman lines in molecules containing the same valence group (*e.g.*, C-H, C=C, and C=O) has led to the association of a vibration frequency with each valence linkage. Hibben<sup>7</sup> lists the characteristic frequency and force constant for several types of linkage. Unfortunately considerable variation in some of these valence frequencies is observed. For example, valence vibrations involving the -C-C- linkage lie between 800 and  $1100\text{ cm}^{-1}$ . In spite of frequent ambiguity in the designation of bands on this basis, the method has been useful in studying chemical structure and the mechanism of polymerization. Hibben's<sup>8</sup> Raman investigation of methyl methacrylate before and after polymerization indicates, by the disappearance of the C=C line, that polymerization is brought about by this group.

The regions of selective absorption in the infra-red correspond roughly to the frequencies of vibration and rotation of the atoms in a molecule. These frequencies usually are calculated by assuming a molecular model in which the atoms are acted upon by central or valence forces and by treating the model as a dynamical system having various normal modes of vibration. A normal vibration in polyatomic molecules does not necessarily take place along interatomic lines, but generally along intermediate axes. Therefore, it is not strictly proper to assign frequencies of polyatomic molecules to particular valence bonds. According to Wall<sup>9</sup> the frequency  $990\text{ cm}^{-1}$  of ethane involves angle bending in the  $\text{CH}_3$  group to a greater extent than displacement of the carbon atoms, even though this frequency is usually assigned to vibrations along the carbon-carbon bond.

\* Reprinted from the *Journal of Applied Physics*, Vol. 12, No. 1, pages 35-40, January 1941.

Recently Whitcomb, Nielsen and Thomas<sup>10</sup> have formulated the most complete theory of the normal modes of vibration of an infinitely long chain composed of  $\text{CH}_2$  groups. They assume a central force model wherein all carbon atoms lie in a plane (but not a straight line) with the hydrogen atoms situated symmetrically along the chain. Three of their normal modes of vibration are shown in Fig. 1, in which the frequencies stated are for  $\text{C}_{11}\text{H}_{24}$ . The vibration  $\nu_2(\sigma\pi)$  is interesting because its frequency  $1463\text{ cm}^{-1}$  in the hydrocarbons usually has been assigned empirically to the deformation vibration  $\nu_4(\pi\sigma)$  of the  $\text{CH}_2$  group. In  $\nu_4(\sigma\sigma)$  there is a combination deformation and carbon-carbon valence vibration. Other normal modes of the hydrocarbons involve twisting and rocking motions of the  $\text{CH}_2$  groups, as well as C-H vibrations. In their application of

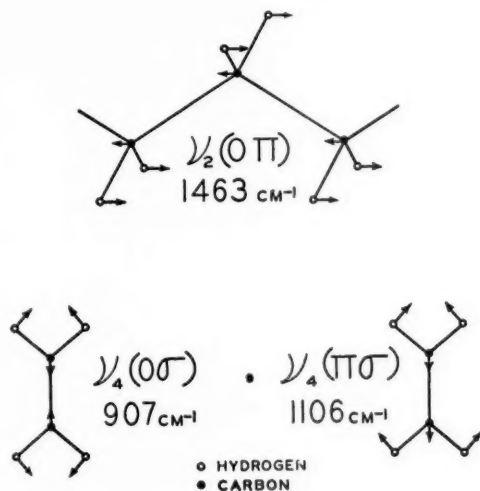


FIG. 1.—Three of the normal vibrations of a long chain paraffin. In  $\nu_2(\sigma\pi)$  a portion of the molecule is viewed nearly perpendicular to the plane containing the carbon atoms; in  $\nu_4(\sigma\sigma)$  and  $\nu_4(\pi\sigma)$  the molecule is viewed along the axis of least moment of inertia.

the theory to  $\text{C}_{11}\text{H}_{24}$  the force constants between the  $h$ th  $\text{CH}_2$  group and the  $(h+2)$  and  $(h-2)$   $\text{CH}_2$  groups are assumed negligible. In spite of this simplification there is good agreement between the observed and calculated frequencies in  $\text{C}_{11}\text{H}_{24}$ .

Considering the useful physical and chemical properties possessed by many long chain polymers, information concerning their structure is of vital importance to the organic chemist, through whose syntheses new products are made possible. Accordingly, it was thought worth while to investigate the infra-red spectra of crude rubber, soft and hard vulcanized rubber, thermoprene (cyclorubber), polyvinylchloride, Neoprene (polychloroprene) and Pliofilm (rubber hydrochloride). The measurements were made at the Mendenhall Laboratory of Physics, Ohio State University.

#### EXPERIMENTAL

Films of the various materials studied were prepared by dissolving them first in a suitable solvent. A wire ring was dipped into this solution, forming a film

of suspended liquid. The solvent was allowed to evaporate, leaving a very thin film of solid within the ring. Films of crude rubber, thermoprene, polyvinylchloride and Neoprene were prepared in this manner, using the solvents indicated in Table I. Rubber films also were made by the dip method from latex. The hard rubber stock was calendered on tin and cured in a mold. The thickness of the various films as measured with an ordinary micrometer, ranged from 0.0037 to 0.0066 cm.

The infra-red transmission of these films was measured in the region between  $2.2\mu$  and  $14.8\mu$  on a Wadsworth-Littrow NaCl prism spectrometer of the type described by Strong and Randall.<sup>11</sup> Radiation from the optical part of the spectrometer was focused on a vacuum thermocouple, which was connected in series with a Leeds and Northrup galvanometer of sensitivity  $0.0045\mu\text{v}/\text{mm}$  for the scale distance used. The ratio of the galvanometer deflection observed when the specimen was placed in front of the spectrometer slit to the deflection observed when the specimen was out of the optical path gives the percentage transmission. Each film was adjusted in the path of the beam to give greatest transmission and least scattering.

The results are plotted in Figs. 2, 3 and 4 as per cent transmission against wave-length and frequency. The curve for  $\text{C}_{11}\text{H}_{24}$  is reproduced here from the work of Whitcomb, Nielsen and Thomas<sup>10</sup> for comparison with rubber. In Table II their calculated frequencies for an infinitely long chain paraffin are compared with those observed in crude rubber. The observed frequencies and relative intensities of the vibration bands in hard vulcanized rubber, soft vulcanized rubber, rubber cured hard in  $\text{S}_2\text{Cl}_2$ , thermoprene, polyvinylchloride, Neoprene and Pliofilm are given in Table III.

## DISCUSSION

A similarity is observed (Fig. 2 and Table II) between the spectra of crude rubber and  $\text{C}_{11}\text{H}_{24}$ , which appears to be more than accidental. The strong C—H valence vibrations,  $\nu_3(\pi\sigma)$  and  $\nu_3(\sigma\sigma)$ , in the region of  $2900\text{ cm}^{-1}$  in  $\text{C}_{11}\text{H}_{24}$  are also present in rubber, but the two weak C—H bands,  $\nu_7(\pi\sigma)$  and  $\nu_7(\sigma\sigma)$ , near  $2300\text{ cm}^{-1}$  are absent in rubber. The band at  $1814\text{ cm}^{-1}$  in  $\text{C}_{11}\text{H}_{24}$ , which is designated as the first harmonic of  $\nu_4(\sigma\sigma)$  at  $907\text{ cm}^{-1}$ , appears to correspond to the  $1681\text{ cm}^{-1}$  band in crude rubber, a first harmonic of the strong vibration at  $846\text{ cm}^{-1}$ . Instead of the band at  $1681\text{ cm}^{-1}$  observed in this work Williams<sup>2</sup> reported a band at  $1725\text{ cm}^{-1}$ , which he designated as the first harmonic of an unobserved fundamental. Also, he observed a band at  $1600\text{ cm}^{-1}$ , a  $-\text{C}=\text{C}-$  vibration according to his assignment. Stair and Coblenz likewise obtained only the one band at  $1681\text{ cm}^{-1}$  for rubber. The same spectra have been obtained in the present work for pale crepe rubber and evaporated latex.

If the band at  $1681\text{ cm}^{-1}$  in crude rubber is due to  $-\text{C}=\text{C}-$  bonds, its intensity should nearly vanish in hard vulcanized rubber, which is supposed to contain very few double bonds. On the contrary, this band is more intense in rubber vulcanized hard with sulfur and with  $\text{S}_2\text{Cl}_2$  than in crude rubber. The bands at  $979$  and  $1550\text{ cm}^{-1}$  in soft vulcanized rubber (Fig. 3), which were also present in the uncured compound, may be due to some curing ingredients. Otherwise, the frequencies and relative intensities in soft vulcanized rubber are the same as those in crude rubber.

The parallel vibration  $\nu_2(\sigma\pi)$  at  $1463\text{ cm}^{-1}$  in  $\text{C}_{11}\text{H}_{24}$  also is found in rubber before and after vulcanization, thermoprene, polyvinylchloride, Neoprene and

TABLE I  
 COMPOUNDING DATA OF INFRA-RED FILMS

Name	Chemical formula	Composition	Solvent	Film		Cure
				Method	Thickness (cm.)	
Crude rubber .....	$\begin{array}{c} \text{H} & \text{H} & \text{H} \\   &   &   \\ -\text{C}- & \text{C}=\text{C}- & \text{C}- \\   &   &   \\ \text{H} & \text{CH}_3 & \text{H} \end{array}$	Pale crepe .....	Gasoline	Dip	0.0037	None
Hard vulcanized rubber....	—	Smoked sheet rubber.. 65.05 Sulfur .....	None	Press	0.0066	130 minutes at 310° F
		Accelerators and softeners .....				
		14.20				
Soft vulcanized rubber....	—	Smoked sheet rubber.. 94.9 Sulfur .....	Gasoline	Dip	0.0061	30 minutes at 206° F in steam
		2.3				
		Stearic acid .....				
		0.9				
		Zinc oxide .....				
		0.9				
		Tetramethylthiuram disulfide .....				
		1.0				
Rubber: S <sub>2</sub> Cl <sub>2</sub> cured hard..	—	35 per cent latex.....	—	Dip	0.0045	48 hrs. in S <sub>2</sub> Cl <sub>2</sub>
Thermoprene .....	—	Cyclorubber .....	Benzene	Dip	0.0053	None
Polyvinylchloride .....	$\begin{array}{c} \text{H} & \text{H} & \text{H} \\   &   &   \\ -\text{C}- & \text{C}- & \text{C}- \\   &   &   \\ \text{H} & \text{Cl} & \text{H} \end{array}$	—	Methyl ethyl ketone	Dip	0.0053	None
Neoprene .....	$\begin{array}{c} \text{H} & \text{H} \\   &   \\ -\text{C}- & \text{C}=\text{C}- \\   &   \\ \text{H} & \text{Cl} \end{array}$	Neoprene type E.....	Benzene	Dip	0.0061	None
Pliofilm .....	$\begin{array}{c} \text{H} & \text{CH}_3 & \text{H} \\   &   &   \\ -\text{C}- & \text{C}- & \text{C}- \\   &   &   \\ \text{H} & \text{Cl} & \text{H} \end{array}$	Commercial sample .....	—	—	0.0040	None

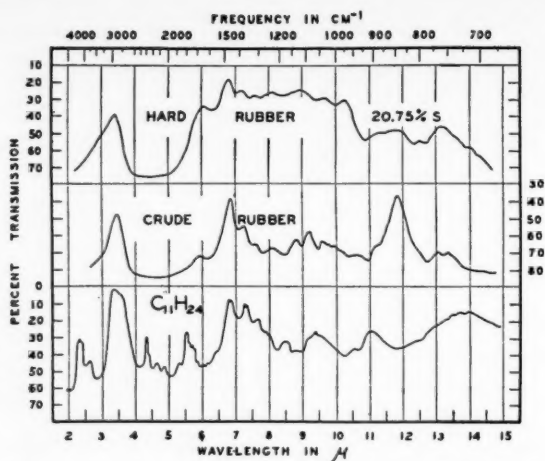


FIG. 2.—Infra-red spectra of  $C_{11}H_{24}$ , crude and hard vulcanized rubber.

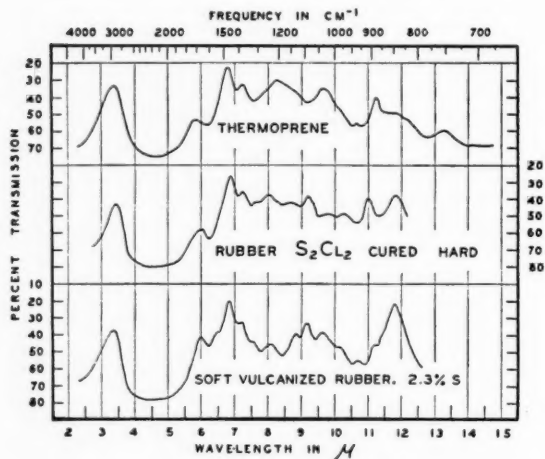


FIG. 3.—Infra-red spectra of thermoprene (cyclorubber), rubber cured 48 hours in  $S_2Cl_2$ , and soft vulcanized rubber.

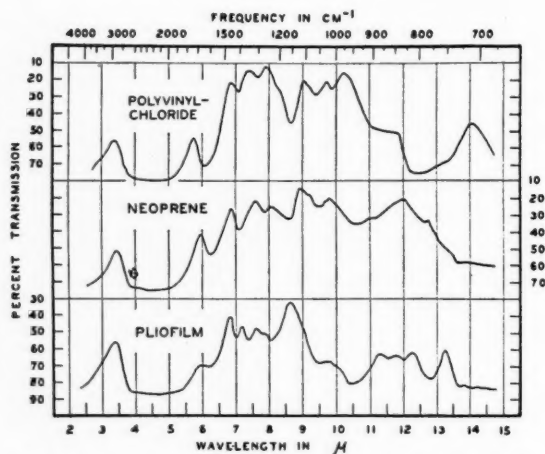


FIG. 4.—Infra-red spectra of polyvinylchloride, Neoprene (polychloroprene) and Pliofilm (rubber hydrochloride).

TABLE II

 COMPARISON OF THE CALCULATED FREQUENCIES OF AN INFINITELY LONG CHAIN  
 PARAFFIN WITH THOSE OBSERVED IN CRUDE RUBBER

Long Chain Paraffin: Calculated				Crude Rubber: Observed				
Wave-length $\mu$	Frequency $\text{cm}^{-1}$	$\text{C}_{11}\text{H}_{24}$ Relative Intensity $I$	Designation	Wave-length $\mu$	Frequency $\text{cm}^{-1}$	Relative Intensity $I$	Probable Origin Designation	Frequency $\text{cm}^{-1}$
2.28	4389	6	$3\nu_2(o\pi)$	—	—	—	—	—
3.54	2926	—	$2\nu_2(o\pi)$	3.45	2899	9	$2\nu_2(o\pi)$	2920
3.60	2778	10	$\nu_3(\pi\sigma)$	—	—	—	$\nu_3(\pi\sigma)$	2778
3.63	2752	—	$\nu_3(o\sigma)$	—	—	—	$\nu_3(o\sigma)$	—
4.31	2320	6	$\nu_1(\pi\sigma)$	—	—	—	—	—
4.40	2273	2	$\nu_1(o\sigma)$	—	—	—	—	—
5.51	1814	5	$2\nu_4(o\sigma)$	5.95	1681	3	$2\nu_4(o\sigma)$	1692
6.84	1463	9	$\nu_2(o\pi)$	6.85	1460	9	$\nu_2(o\pi)$	1463
7.28	1374	8	$2\nu_6(\pi\sigma) + \nu_6(o\sigma)$	7.28	1374	7	$2\nu_6(\pi\sigma) + \nu_6(o\sigma)$	1460
7.39	1354	5	$\nu_6(o\pi)$	7.61	1314	5	$\nu_6(o\pi)$	1308
8.28	1208	4	$2\nu_6(o\sigma)$	8.10	1234	5	$2\nu_6(o\sigma)$	1200
—	—	—	—	8.82	1134	6	—	—
9.04	1106	5	$\nu_4(\pi\sigma)$	9.17	1091	7	$\nu_4(\pi\sigma)$	1106
9.63	1038	5	$\nu_5(o\sigma)$	9.65	1036	6	$\nu_5(o\sigma)$	1038
10.11	989	4	$\nu_6(\pi\sigma) + \nu_6(o\sigma)$	10.70	935	3	—	—
—	—	—	—	11.15	897	3	—	—
11.03	907	8	$\nu_4(o\sigma)$	11.82	846	10	$\nu_4(o\sigma)$	907
13.00	770	4	$2\nu_6(\pi\sigma)$	13.25	755	5	$2\nu_6(\pi\sigma)$	770
16.56	604	6	$\nu_6(o\sigma)$	16.66*	600*	6	$\nu_6(o\sigma)$	604
25.97	385	4	$\nu_6(\pi\sigma)$	23.2*	430*	4	$\nu_6(\pi\sigma)$	385

\* A. J. Wells, J. App. Phys. 11, 137 (1940).

Pliofilm at very nearly the same frequency. This vibration is one in which the carbon and hydrogen atoms move along the axis of least moment of inertia of the molecule in opposite directions. The band at  $1374\text{ cm}^{-1}$  in  $\text{C}_{11}\text{H}_{24}$  is said to be a combination band, while  $\nu_6(o\pi)$  at  $1354\text{ cm}^{-1}$  involves a twisting motion of the  $\text{CH}_2$  groups. Stair and Coblenz and the writer find a band at  $1234\text{ cm}^{-1}$  in rubber, which Williams did not observe. The angle deformation vibration  $\nu_4(\pi\sigma)$  at  $1106\text{ cm}^{-1}$  in  $\text{C}_{11}\text{H}_{24}$  also may be active in rubber, but its frequency is uncertain. Very likely the band at  $846\text{ cm}^{-1}$  in rubber corresponds to the C—C vibration  $\nu_4(o\sigma)$  at  $907\text{ cm}^{-1}$  in  $\text{C}_{11}\text{H}_{24}$ .

Many bands in vulcanized hard rubber appear at the same frequencies as in crude rubber, but the region  $950\text{ cm}^{-1}$  to  $1700\text{ cm}^{-1}$  is greatly intensified by vulcanization. In general, new vibrations characteristic of vulcanization (sulfur and new —C—C— bonds within or between rubber molecules) may be expected at frequencies below  $1000\text{ cm}^{-1}$ . The —C—S— linkage is reported<sup>7</sup> to have a characteristic frequency at  $675 \pm 25\text{ cm}^{-1}$ , but no band is observed here in vulcanized rubber. Absorption from —S—S— linkages at about  $500\text{ cm}^{-1}$ , as in the polysulfides, is beyond the range of the present work. The new band at  $976\text{ cm}^{-1}$  in hard rubber may arise from =C=S linkage vibrations, which are supposed to obtain at  $1072\text{ cm}^{-1}$ .

The new band at  $909\text{ cm}^{-1}$  in rubber cured in  $\text{S}_2\text{Cl}_2$  (Fig. 3) cannot be identified with any of the frequencies of  $\text{S}_2\text{Cl}_2$ . The spectrum of thermoprene is similar to that of crude rubber, but it also has new bands at  $891$ ,  $1036$  and  $1205\text{ cm}^{-1}$ , which cannot be identified empirically as valence vibrations.

TABLE III  
OBSERVED FREQUENCIES AND ESTIMATED RELATIVE INTENSITIES OF HIGH POLYMERS

Hard vul- canized rubber			Soft vul- canized rubber			Rubber: S <sub>2</sub> Cl <sub>2</sub> cured hard			Thermoprene			Polyvinylchloride			Neoprene			Pliofilm		
Wave- length $\mu$	Fre- quency cm <sup>-1</sup>	Inten- sity I	Wave- length $\mu$	Fre- quency cm <sup>-1</sup>	Inten- sity I	Wave- length $\mu$	Fre- quency cm <sup>-1</sup>	Inten- sity I	Wave- length $\mu$	Fre- quency cm <sup>-1</sup>	Inten- sity I	Wave- length $\mu$	Fre- quency cm <sup>-1</sup>	Inten- sity I	Wave- length $\mu$	Fre- quency cm <sup>-1</sup>	Inten- sity I	Wave- length $\mu$	Fre- quency cm <sup>-1</sup>	Inten- sity I
3.41	2933	10	3.39	2950	9	3.41	2933	9	3.38	2959	10	3.40	2941	5	3.44	2907	4	3.39	2950	8
6.08	1645	6	5.96	1678	5	5.98	1672	4	5.80	1724	4	5.75	1740	4	5.95	1681	6	5.93	1686	3
6.84	1462	10	6.45	1550	4	6.86	1458	10	6.80	1471	10	6.85	1460	7	6.86	1458	8	6.82	1466	9
7.25	1379	8	7.23	1383	7	7.25	1379	8	7.23	1383	7	7.40	1351	7	7.60	1316	9	7.18	1393	7
7.60	1316	7	7.56	1323	5	7.60	1316	6				7.95	1258	9	8.10	1235	8	7.60	1316	6
8.08	1238	8	8.07	1239	5	8.00	1250		8.30	1205	9	8.35	1200	3	8.95	1117	10	7.90	1265	5
9.00	1111	9	8.82	1134	6	8.68	1152	6				9.06	1104	8	8.95	1117	10	8.65	1156	10
9.65	1036	7	9.17	1091	7	9.18	1089	8							9.20	1087	6	9.80	1020	5
10.25	976	7	9.63	1038	6	9.75	1026	3	9.65	1036	8	9.73	1028	8	9.80	1020	8	10.20	980	3
			10.22	979	4	10.23	978	4				10.25	976	9						
			10.75	930	3				10.63	941	1									
11.20	893	3	11.15	897	4	11.00	909	6							11.00	909	3	11.30	885	6
11.82	846	4	11.82	846	10	11.81	847	7	11.22	891	7									
12.50	800	2							12.00	834	6	11.55	866	6	11.95	837	10	11.80	848	6
13.20	758	5							13.25	755	3	14.05	712	7	12.75	784	7	12.30	813	7
																		13.25	755	8



The spectra of the long chain polymers, polyvinylchloride, polychloroprene and rubber hydrochloride, might be expected to differ widely from those of the hydrocarbons because they all contain the heavy atom, chlorine. Many new, intense bands appear in polyvinylchloride and the commercial materials known as Neoprene and Pliofilm (Fig. 4) which readily distinguish each of these substances from rubber and the hydrocarbons. The C—H bands in the region  $2900\text{ cm}^{-1}$  of polyvinylchloride and Neoprene are less intense than those in the saturated paraffins. The bands at  $1740\text{ cm}^{-1}$  in polyvinylchloride,  $1681\text{ cm}^{-1}$  in Neoprene and  $1686\text{ cm}^{-1}$  in Pliofilm are believed to be partly harmonics of fundamentals in the region of  $850\text{ cm}^{-1}$ . The vibration  $\nu_2(\sigma\pi)$  at  $1460\text{ cm}^{-1}$  remains almost unchanged from its position in the hydrocarbons in all three of these substances. A C—Cl vibration, such as is observed in methylchloride at  $732\text{ cm}^{-1}$ , may be present at  $712\text{ cm}^{-1}$  in polyvinylchloride,  $784\text{ cm}^{-1}$  in Neoprene and  $755\text{ cm}^{-1}$  in Pliofilm.

All the bands of polyvinylchloride in the present work correspond directly with those obtained by Stair and Coblenz<sup>3</sup> for polyvinylacetate in the region between  $2.2\mu$  and  $11\mu$ . This agreement is not surprising in view of their known similarity of chain structure. Moreover, it indicates that the perturbation of the chain vibrations produced by the acetate side group in polyvinylacetate and by the chlorine in polyvinylchloride is roughly the same. On the other hand, the infra-red spectra of polystyrene (polyvinylbenzene) measured by Stair and Coblenz<sup>3</sup> shows that it has a different chain structure from polyvinylchloride and polyvinylacetate.

The assignments of the vibration bands of complicated molecules to particular valence bonds is not only uncertain, but also there remains a large number of bands unexplained. Calculation of the normal modes of vibration for each of these high polymers using the method of Whitcomb, Nielsen and Thomas might account for their observed spectra and give valuable information concerning their structure. The similarity between the spectra of rubber and  $\text{C}_{11}\text{H}_{24}$  between  $2.2\mu$  and  $14.8\mu$  suggests that the bands for rubber in this region arise from interatomic vibrations of relatively short sections of the chain. The low frequency vibrations (below  $700\text{ cm}^{-1}$ ) of these high polymers, which are characteristic of interlocking and cross bonding, should be investigated in order to obtain information about the molecular arrangement.

The author is indebted to H. H. Nielsen of Ohio State University for valuable discussions.

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# RELATION BETWEEN MOLECULAR WEIGHTS AND PHYSICAL PROPERTIES OF RUBBER FRACTIONS \*

G. GEE and L. R. G. TRELOAR

As high elasticity is a property possessed only by substances of high molecular weight, it is of interest to enquire into the relation between the elastic properties of a highly elastic material such as rubber and its molecular weight. An investigation on these lines has been made possible through the work of Bloomfield and Farmer<sup>1</sup>, who have succeeded in separating natural rubber into fractions having different average molecular weights. The more important physical properties of these fractions have been examined with the object of determining which of the properties are dependent on molecular weight and which are not. Fairly extensive observations were made on the fractions from latex rubber referred to as Nos. 2, 3 and 4 by Bloomfield and Farmer, and some less extensive observations were carried out on the less oxygenated portion of fraction No. 1 obtained from crepe rubber (called hereafter 1B). Before considering these experimental results, and their relation to the molecular weights of the fractions, it will be necessary to refer briefly to the methods used for the molecular-weight determinations, and to discuss the significance of the figures obtained.

**MOLECULAR WEIGHT DETERMINATIONS.**—The osmotic and viscosity molecular weights were determined by the methods described in a recent paper<sup>2</sup>. Fractions No. 1B, No. 2 and No. 3 were dissolved in a mixture of benzene and 15 per cent of methyl alcohol to give solutions of approximately 1 per cent concentration. In preparing these solutions, the mixtures of rubber and solvent, after being carefully degassed by successively cooling in liquid air, pumping to a pressure of less than  $10^{-4}$  mm., and warming up, were sealed *in vacuo* and shaken mechanically until solution was complete. Fraction No. 1 dissolved almost at once, No. 2 after standing overnight and shaking for a short time, but No. 3 required 2 to 3 days to give a homogeneous dispersion. Osmotic pressures of these 1 per cent solutions were measured, and used to calculate the osmotic molecular weights. Intrinsic viscosities<sup>3</sup> were measured at a series of concentrations (chosen to give specific viscosities between 0.2 and 0.05), and the values at infinite dilution obtained by extrapolation. Using the Staudinger constant previously calculated for a mixture of benzene and 15 per cent methyl alcohol, these figures enabled the viscosity molecular weights to be calculated.

Fraction No. 4 presented more difficulty. It was supplied as a 0.25 per cent solution in a mixed solvent whose precise composition was unknown. If this solution was evaporated to dryness, even *in vacuo* at room temperature, the residue was insoluble in all the usual solvents. A portion of the solution was therefore diluted to ten times its volume with benzene, and its viscosity was determined. To obtain a solvent of similar composition for comparison, the whole of the solvent from 10 cc. of the original solution was distilled off, and made up to 100 cc. with benzene: this solvent was used in further dilutions of the viscosity

\* Reprinted from *Transactions of the Institution of the Rubber Industry*, Vol. 16, No. 4, pages 184-197, December 1940.

solution. In this way the intrinsic viscosity at infinite dilution was found. To convert this to a molecular weight, the Staudinger constant of the solvent had to be derived by measuring the intrinsic viscosity in it of some substance of known molecular weight: crepe rubber was actually employed. Expressing the concentration of solutions in grams per 100 cc., the intrinsic viscosities at infinite dilution of crepe rubber and of fraction No. 4 were found to be 6.1 and 6.4, respectively. Taking the viscosity molecular weight of crepe rubber as  $3.4_5 \times 10^5$ , the Staudinger constant for the mixed solvent was  $5.6_5 \times 10^4$ , and the molecular weight of fraction No. 4 was  $3.6 \times 10^5$ . No osmotic molecular weight was measured for this fraction, since it was not possible to obtain a suitable solution. The complete results, with the estimated probable errors, are given in Table I.

DISPERSITY OF THE FRACTIONS.—These figures, together with the details of the fractionation procedure<sup>1</sup>, enable the authors to draw some tentative conclusions regarding the nature and dispersity of the fractions. On the basis of the fractionation work alone, two possible views of the molecular distribution in rubber may be entertained. The fractions isolated may represent well defined peaks in the distribution, or may be only arbitrarily selected molecular-weight bands cut from a continuous distribution. In the latter case the relative weights

TABLE I  
VISCOSITY AND OSMOTIC MOLECULAR WEIGHTS  
Molecular weight  $\times 10^{-5}$

Fraction	Viscosity	Osmotic
No. 1B .....	$0.63 \pm 0.02$	$0.66 \pm 0.03$
No. 2 .....	$2.4 \pm 0.1$	$2.1 \pm 0.3$
No. 3 .....	$3.5_5 \pm 0.1$	$3.5 \pm 0.2$
No. 4 .....	$3.6 \pm 0.3$	—

of the fractions and their mean molecular weights would be changed by small alterations in the petrol ether-acetone ratios at which cuts were made in the fractionation. Experimentally it is doubtful whether it would be practicable to change the solvent composition by sufficiently small amounts, for it can be seen from curve B of Figure 2 that, as the high petrol-ether concentrations were approached, small additions of petrol-ether would bring into solution material covering a wide range of molecular weights.

It has been pointed out elsewhere<sup>2</sup> that the agreement between the osmotic and viscosity molecular weights of a material of linear structure is evidence of the substantial homogeneity of the material. In applying this argument to fractions Nos. 1B, 2 and 3, it is necessary to consider carefully both the basis of the molecular weight determinations and the conclusions which may safely be drawn. The osmotic molecular weights are absolute values, but viscosity data give only relative figures, which in the present case have been standardized by reference to a molecular weight determination from ultra-centrifuge data. If the standardization is in error, the apparent agreement would of course be fortuitous. Although no independent check has yet been possible, it is believed that the standard used cannot have been seriously in error since, in a large number of molecular weight measurements on rubber derivatives, the only cases in which the osmotic molecular weights exceeded the viscosity values were those in which there was reason to believe that some cyclization of the rubber structure had occurred. For the present, therefore, it is concluded that the osmotic and viscosity molecular weights agree, within the limits of experimental error, for each of the first three

fractions. This, however, does not imply that these fractions are even approximately monodisperse, because comparatively small experimental errors may cover a rather wide variation of molecular weight, as the following considerations will indicate. In the absence of any evidence about the probable molecular distribution within the fractions<sup>4</sup>, Lansing and Kraemer's suggestion<sup>5</sup> may be followed, and the distribution represented for the purposes of this discussion by an error function, in which the weight  $dw$  of material having a molecular weight between  $M$  and  $M + dM$  is represented in terms of a single parameter  $\beta$  by the equation:

$$dw = \frac{W}{M_0 \beta \sqrt{\pi}} e^{-y^2} dM \quad (1)$$

where  $W$  is the total weight of material

$$y = 1/\beta \log_e (M/M_0).$$

$M_0$  = the molecular weight present to the greatest extent.

The viscosity and osmotic molecular weights may be calculated by the equations:

$$M_{\text{osmotic}} = \frac{\sum n_i M_i}{\sum n_i}$$

$$M_{\text{viscosity}} = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

where  $n_i$  is the number of molecules having a molecular weight  $M_i$  and the summations are taken over all values of  $i$ . Employing equation (1) to define  $n_i$  as a function of  $M_i$ , and summing, it may be shown that the viscosity and osmotic molecular weights are given by:

$$M_{\text{osmotic}} = M_0 e^{0.25\beta^2}$$

$$M_{\text{viscosity}} = M_0 e^{0.75\beta^2}$$

Fraction No. 3 appears to be the most sharply defined experimentally; taking the limits of error given in Table I, the maximum possible value of  $\beta$  is 0.45, and the most probable value 0.2. Taking  $\beta = 0.2$ , equation (1) has been employed to calculate the molecular distribution of fractions 2 and 3. In Figure 1 the ordinates are proportional to the weight of material found within a given narrow band of molecular weights and the areas under the curves to the total weights of the two fractions found experimentally. The dotted curve is the sum of the two separate curves. It is not suggested that these curves bear any necessary relation to the actual molecular distribution in the fractions, but they lead to two important conclusions.

First, the molecular weight evidence is not sufficient for it to be concluded that the fractions are monodisperse; although the fractions cannot contain large amounts of material of very high or very low molecular weight, there may well be a considerable spread of molecular weights about the mean.

Secondly, the separation between fractions Nos. 2 and 3 is so small that both might actually be embraced in a continuous molecular weight distribution, in the manner indicated by the dotted line in Figure 1.

The analytical evidence<sup>1</sup> shows Nos. 2 and 3 to be essentially pure hydrocarbons of the composition:  $(C_6H_8)_x$ . The lowest fraction, No. 1B, still contained about 0.5 per cent of oxygen, which might have been sufficient to affect its solubility

in petrol ether-acetone mixtures. It is not, however, unreasonable to suggest that the composition of the mixture which just dissolved it would not differ greatly from that required to dissolve a pure hydrocarbon of the same molecular weight. The high fraction, No. 4, presents more difficulty, in that it was not obtained entirely free from nitrogen, although, in the sample actually used in the present work, the nitrogen content had been reduced to 0.03 per cent. It is not certain whether this small amount is sufficient to account for the greatly diminished solubility of this fraction, but the difference of molecular weight between No. 3

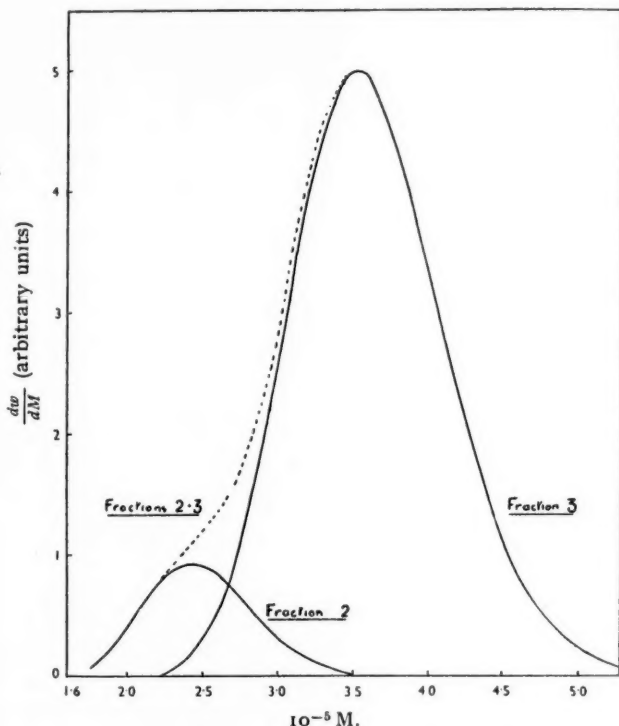


FIG. 1.—Theoretical molecular weight distribution.  
Curves for rubber fractions.

and No. 4 is certainly too small in itself to account for their separation. Schulz<sup>6</sup> has shown that the data of Staudinger and Heuer<sup>7</sup> for the variation of critical solvent composition with molecular weight in the case of a series of polystyrenes can be represented accurately by the equation:

$$x = \alpha + \beta/M$$

where  $x$  is the proportion of alcohol in the mixture of benzene and alcohol,  $M$  the molecular weight of the polystyrene, and  $\alpha$  and  $\beta$  are constants. If this relationship holds for the present fractions, a plot of the percentage of acetone in the critical solution mixtures against  $1/M$  should be linear. The data are shown in Table II and plotted in Figure 2 (Curve A).

The first three fractions fall reasonably into line with the theory of Schulz, but the separation of No. 4 must evidently be ascribed to some factor other than molecular weight. Figure 2 suggests that a mixture containing 38 per cent of

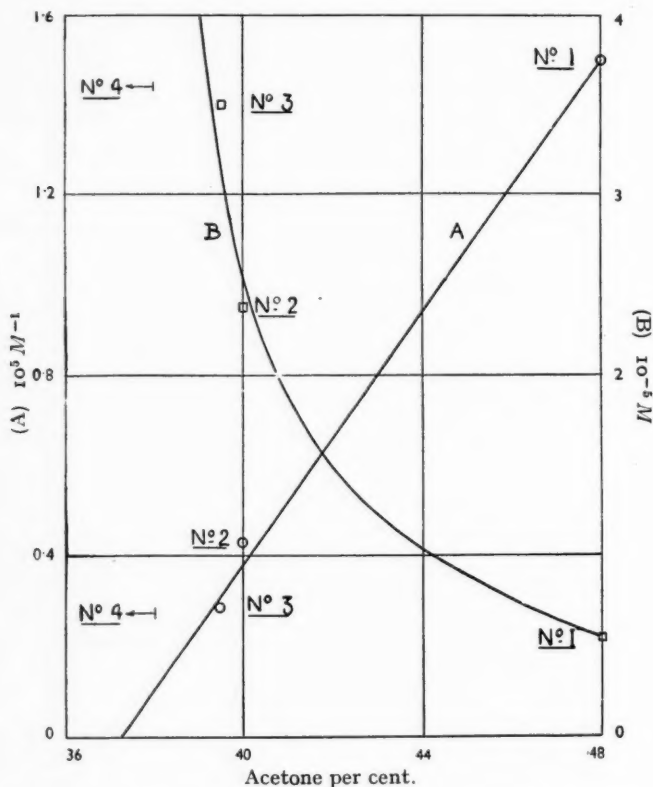


FIG. 2.—Effect of molecular weight of fraction on composition of petrol-ether/acetone mixtures required for solution.

TABLE II

SOLUBILITY OF FRACTIONS IN PETROL ETHER-ACETONE MIXTURES AT 20° C.

Fraction	Percentage of acetone in critical solubility mixture	$10^5/M$
No. 1B .....	48	1.55
No. 2 .....	40	0.43
No. 3 .....	39.5	0.29
No. 4 .....	<38	0.28

acetone would dissolve a rubber of molecular weight  $10^6$ ; the insolubility of No. 4 in this mixture therefore requires some special explanation. The possible role of its nitrogen content in thus diminishing its solubility is difficult to assess, but it may be noted that solutions of the corresponding fraction from crepe rubber



(containing 2.7 per cent nitrogen) were difficult to filter. Even when diluted to a concentration of 0.02 gram per 100 cc., the solution speedily blocked a Jena G2 filter, showing the presence of large aggregates. It is possible that smaller aggregates were present in the solution of No. 4 fraction: these would contribute but little to the viscosity, and thus lead to an underestimate of the molecular weight. Pending an ultracentrifugal examination, it is impossible to be certain as to the nature of solutions of this fraction, a point which must be borne in mind in considering the relation of its apparent properties to its apparent molecular weight.

**PHYSICAL PROPERTIES OF THE FRACTIONS.**—The physical properties included in this investigation were the following:

1. The tension, and its time variation, at various elongations.
2. The double refraction at various elongations (which gives a measure of the amount of crystallization).
3. The elastic retraction.
4. The plastic flow accompanying elastic deformation.
5. The low-temperature limit of elastic extensibility.

**Experimental methods and data.**—Films were prepared from the original solutions containing the rubber fractions (together with a little antioxidant) by drying on mercury. The methods of examination followed the lines already described<sup>8</sup>. Specimens cut from the films were stretched instantaneously to various extensions, and the tension and birefringence simultaneously observed over a period of one hour. The tension was then released, and the subsequent recovery at 25° C was followed for 20 hours or more. The further retraction on raising the temperature was then examined, after which any residual elastic strain was removed by treating the specimens (floating on mercury) with suitable benzene-alcohol mixtures. This final treatment had to be omitted in the case of Nos. 1b and 2 because of their mechanical weakness. The extensions remaining after the complete removal of the elastic strain were taken as a measure of plastic flow. The low-temperature limit of elastic extensibility was determined by cooling the specimen to below -70° C, and then allowing the temperature to rise slowly until an extension of 100 per cent was produced by a weight of 1 kilogram.

1. *Tensile behavior.*—The variations in tension observed when fractions Nos. 2, 3 and 4 were stretched to various elongations at 25° C are shown in Fig. 3. The maximum tension supported by No. 3 was about 12 times that by No. 2, although the maximum elongation was about the same. The elastic part of the deformation was, however, much lower for No. 2, on account of its greater plastic flow. Differences in tension between No. 3 and No. 4 were relatively slight, though there was a significantly smaller fall in tension immediately after stretching in the case of No. 4. This fraction also appeared to possess a somewhat higher range of extensibility. Tension curves were not obtained for the No. 1b fraction, which was rather sticky and difficult to handle at room temperature. At 0° C its maximum extensibility was only about 450 per cent.

2. *Birefringence.*—Birefringence in stretched rubber has been shown to be simply related to the amount of crystalline material formed on stretching at a temperature of 25° C or higher<sup>9</sup>. Figure 4 shows a plot of the birefringence at the end of one hour against elongation for fractions Nos. 2, 3 and 4. The curve for No. 3 is quantitatively similar to the curves for total rubber. The elongations required to produce appreciable crystallization were higher for No. 4 than for No. 3, and at 50° C the maximum crystallization in No. 4 was not so high. At



25° C the birefringence-elongation curve for this fraction became flat beyond about 1000 per cent elongation; this unusual phenomenon will be referred to in connection with the plastic flow. For No. 2 fraction, a much higher elongation

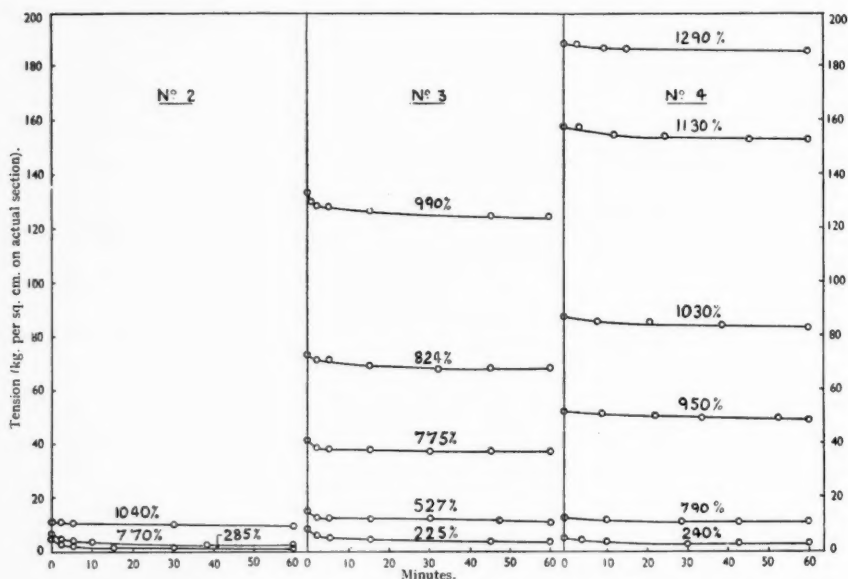


FIG. 3.—Tension curves at constant extension for rubber fractions 2, 3 and 4.

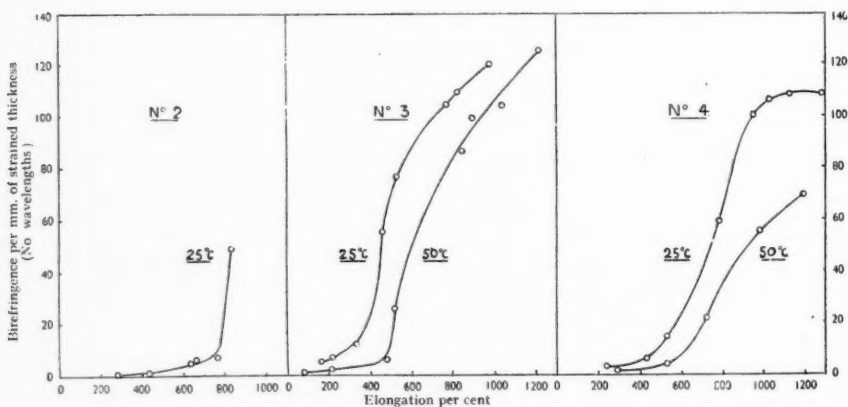


FIG. 4.—Birefringence at end of one hour's extension to various elongations of rubber fractions 2, 3 and 4.

(800 per cent) was required to produce crystallization at 25° C, and the maximum amount of crystallization was considerably less than in Nos. 3 and 4 at this temperature. No measurements of birefringence were made with the No. 1B fraction.

3. *Elastic retraction*.—Fractions Nos. 2, 3 and 4 each showed the two distinct types of recovery phenomena exhibited by total rubber. With specimens extended to an elongation less than that necessary to produce appreciable crystallization the retraction was gradual, and each increase in temperature caused a further reduction in length. If, however, the elongation was sufficient to produce crystallization (as determined optically), there was little retraction until a certain temperature was reached, after which almost the whole of the recovery occurred within a range of temperature of 2° C. The temperatures at which this recovery occurred for crepe rubber and for three of the fractions, are given in Table III. No. 1b did not show the critical-temperature phenomenon.

4. *Plastic flow*.—Plastic flow data for Nos. 2, 3 and 4 are given in Figure 5. When plotted against elongation, the plastic flow in each case shows a maximum, and there is a close correspondence between the positions of the respective maxima and the elongations at which the birefringence measurements indicate the onset of crystallization. Further evidence of this correlation between the mechanical and optical properties is provided by the anomalous behavior of fraction No. 4, which at 25° C showed a minimum in the flow-elongation curve at the same elongation as that at which the birefringence ceased to increase. There were indications of this effect also at 50° C.

TABLE III  
CRITICAL RECOVERY TEMPERATURES

Fraction	Temp. of stretching	Elongation (Per cent)	Recovery (Temp.)
Crepe rubber .....	25° C	640	29.5° C
No. 2 .....	25°	1040	30.5°
No. 3 .....	25°	950	29°
No. 4 .....	25°	720	29°

The plastic flow data of No. 3 fraction are very similar to those already found for crepe rubber<sup>8</sup>. Apart from the anomaly referred to, No. 4 shows no marked difference from No. 3, though it appears to be rather less sensitive to temperature changes. In No. 2, on the other hand, the flow differs in order of magnitude, the maximum being about 30 times as high. The only figure obtained for No. 1b at 25° C was at 300 per cent elongation, where the plastic flow amounted to 70 per cent, *i.e.*, about twice as great as for No. 2 at the same elongation. At 0° C, the flow rose from 0 per cent at 120 per cent elongation to 22 per cent at 450 per cent elongation, but the flow-elongation curve showed no maximum.

5. *The low-temperature limit of elastic extensibility*.—This is the temperature at which rubber loses its elastic properties and freezes to a glassy state, quite distinct from the crystalline state brought about by more moderate cooling. This change is presumably the same as that found by Wood, Bekkedahl and Peters<sup>10</sup> from their study of thermal expansibility to occur in both amorphous and crystalline rubber at about -69° C, and referred to by them as a second-order transition. The results of observations made on the four fractions and on crepe rubber are given in Table IV.

GENERAL DISCUSSION.—It is clear from the foregoing presentation of data for the fractions that some of the physical properties examined show a marked dependence on molecular weight, whereas others are independent of it. It may therefore be useful to summarize the results under the headings: (1) properties common to all fractions, and (2) properties in which the fractions differ.

(1) *Properties common to all fractions.*

(a) *Retraction temperature.*—The temperature at which retraction took place after an extension sufficient to produce crystallization was the same for all the fractions and for total rubber. This temperature may be regarded as defining the melting point of the crystals, which is thus shown to be independent of the length of the molecule.

(b) *Low-temperature elastic limit.*—This temperature may be related either to the forces between atoms in the molecular chain which might influence the power of rotation about single bonds, or to the forces between neighboring molecules, which might affect the freedom of movement of a given chain among its neighbors. In either case these forces would not be expected to depend on the length of the molecule. The data are in agreement with this expectation.

TABLE IV  
LOW-TEMPERATURE LIMITS OF ELASTICITY

Fraction	Low-temp. limit
Crepe rubber .....	−65.5° C
No. 1B .....	−69°
No. 2 .....	−67°
No. 3 .....	−68.5°
No. 4 .....	−68°

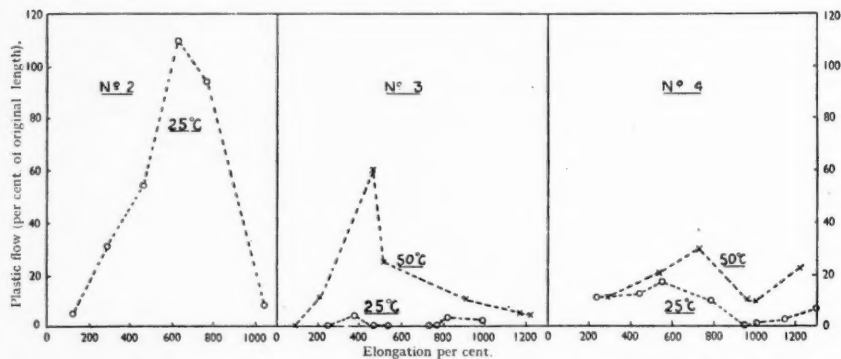


FIG. 5.—Plastic flow on holding rubber fractions Nos. 2, 3 and 4 for one hour at various elongations.

(2) *Properties in which the fractions differ.*

(a) *Plastic flow.*—Plastic flow is the property most directly connected with the internal slippage of molecules, which takes place as a result of an extension. It is fundamentally related to tensile and crystallization phenomena. Thus, if the flow is large, the internal tension on the molecules is quickly released; the molecules therefore are not likely to be strongly pulled into the direction of the extension, and both the tension and the crystallization will consequently be low. If, as seems probable, the mobility of the molecules is limited by their mutual entanglements, the increasing complexity and permanence of such entanglements with increasing molecular weight would be expected to lead to a corresponding reduction in plastic flow. This effect is well shown by the data for fractions Nos. 1B, 2 and 3.

(b) *Tensile behavior*.—Comparison of the data for No. 2 and No. 3 fractions shows that the material of higher molecular weight is capable of supporting a much higher tension.

(c) *Crystallization*.—No. 1b fraction showed none of the phenomena associated with crystallization. In No. 2, crystallization was relatively weak, and in Nos. 3 and 4 it was strong. Crystallization is thus seen to change in the opposite sense to plastic flow.

(d) *Range of extensibility*.—The statistical theory in its present state of development throws little light on the question of the maximum extensibility to be expected from a given high-molecular material. From Kuhn's theory<sup>11</sup> the most probable length of a molecule comprising  $N$  freely rotating links is proportional to  $N^{1/2}$ . For a rubber of molecular weight 250,000, the stretched length on this basis would be in the neighborhood of 100 times the unstretched length, and a molecular extensibility of 10 times would be possible with a molecular weight as low as 2500. This reasoning suggests that the smaller extensibility observed with No. 1b fraction, *i.e.*, 450 per cent, compared with 1000 per cent for No. 3, is due, not so much to a reduction in the extensibility of the molecule itself, as to the increased plastic flow resulting from the reduction of intermolecular entanglement, leading to breaking of the specimen before the molecules are fully extended.

**GENERAL CONCLUSION.**—It is interesting to observe that the physical properties of No. 3 fraction are remarkably similar to the physical properties of total crepe rubber, in spite of the smaller range of molecular weight present in the fraction. This shows that the observed elastic properties of rubber are not dependent on the presence either of a low-molecular component or of a "gel skeleton". It shows also that the non-rubber components of crude rubber play no significant part in determining the fundamental elastic and other mechanical properties displayed by this material.

**ACKNOWLEDGMENT.**—The authors desire to acknowledge the helpful cooperation of J. K. Roberts, of the Colloid Science Laboratory, Cambridge, in the course of this work, and the assistance of A. W. C. Fuller in carrying out the experiments. The work forms part of the program of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

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- <sup>2</sup> Gee, *Trans. Faraday Soc.* **36**, 1163, 1171 (1940).
- <sup>3</sup> The intrinsic viscosity  $[\eta]$  is defined as  $(1/c) \log_e (1 + \eta_{sp})$ , where  $\eta_{sp}$  is the specific viscosity of a solution of concentration  $c$ .
- <sup>4</sup> It is hoped shortly to submit these fractions to ultracentrifugal examination.
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# FRACTIONATION OF RUBBER

G. F. BLOOMFIELD and E. H. FARMER

## A DISCUSSION OF THIS PAPER \*

H. P. Stevens wrote that he had read with interest the above paper and desired to contribute the following observations.

The authors refrained from drawing conclusions from the varying nature and proportions of the fractions in the three typical rubbers of which they gave the distribution in three tables. The impression was obtained that those differences resulted from differences in the nature of the three types, either partly chemical or physical (molecular weight variations), or both.

It was suggested by the writer that the main differences were of a different nature, and resulted from differences in the coarser structure of the specimens. It would be noted that "crepe rubber" (Table I) was rubber prepared by milling wet or semidry coagulum. "Latex rubber" (Table II) was acetone-coagulated after purification, and "dried-fresh-latex film" (Table III) was neither milled nor purified nor coagulated. The three specimens therefore corresponded to three dissimilar types of raw rubber. They would consequently possess different types of macrostructure. Rubber, however prepared, was not merely a mass of hydrocarbon with nitrogen and other accessory substances homogeneously distributed therein. The distribution was of a structural character. In latex, the hydrocarbon particles were surrounded by a nonhydrocarbon sheath of adsorbed material, and there was no reason to suppose that separation of the coagulum from the serum resulted in the removal, or even the rupture of this sheath, unless the physical conditions favored such action. Hence dried latex or dried coagulum, if mechanical disturbance were avoided, should consist of discrete particles of hydrocarbon separated by thin septae of nonhydrocarbon. No doubt it was impossible or difficult to obtain dry rubber without some damage to the particle sheath. Nevertheless in unmilled rubber the particles remained to a large extent intact in a honeycomb structure. This might be seen by swelling small cuttings of smoked sheet rubber in a solvent, such as benzene. Infiltration of solvent caused the particles to swell. The sheaths were partially split or burst, but the smoke which stained predominately the non-rubber, caused the honeycomb structure to be visible to the naked eye or by means of a simple lens. A few photographs illustrating the structure were published as far back as 1925<sup>1</sup>. For this reason unmilled rubber remained swollen but partly undispersed, even in a large volume of benzene, over a period of years; in fact an equilibrium was reached. Successive treatment with solvent did, however, eventually remove almost the whole. On the other hand, crepe rubber, which had been milled in course of preparation, behaved differently, and dissolved almost completely in many solvents or solvent mixtures, given time, even when shielded from light. These remarks might appear elementary, but the relationship of milled and unmilled rubber, corresponding to crepe and dried coagulum or latex film, was frequently lost sight of. The influence of this macrostructure on the relative proportion of the last fractions in the Tables was apparent and unescapable. Crepe rubber (Table I) gave a relatively large "high fraction"

\* Reprinted from *Transactions of the Institution of the Rubber Industry*, Vol. 16, No. 5, pages 276-282, February 1941. The original paper of Bloomfield and Farmer appears in *RUBBER CHEMISTRY AND TECHNOLOGY*, Vol. 14, No. 1, pages 1-14, January 1941.

and a negligible "insoluble residue" (1.8 per cent), for in this rubber the sheaths surrounding the particles were broken up by milling, permitting ready dispersion of the hydrocarbon. The latex rubber (Table II) contained particles with emaciated sheaths as a result of the creaming process, which removed the bulk of the nitrogen present, probably as a protein, forming one of the most important if not the main constituent of the sheath. There was no milling, and the sheaths were substantially intact, although exceptionally weak and tenuous. Consequently the "high fraction" was smaller, and the undissolved residue, "amounting to just over 20 per cent of the whole", was much larger. Finally the air-dried latex films (Table III) gave the largest insoluble residue (36.0 per cent) because the particle sheaths were not emaciated by purification, or broken up by milling, but remained intact, thus presenting a formidable barrier to the access of the solvent to the hydrocarbon particles.

It might well be that the oxidative degradation of gel rubber to yield sol rubber, as postulated by Kemp and Peters, was an oxidation, not of the hydrocarbon, but of minute protective residues remaining in the gel rubber. It was doubtful if gel rubber had ever been entirely freed from nitrogen. Apart from this, it might contain carbohydrate components with physical properties of such a nature as to form solvent-resisting protective films. For some years the writer has had in mind the possibility of the presence in the protective film or sheath of adsorbed nonrubber component of a cellulose, perhaps a hemicellulose, which the accepted purification processes would not completely remove. Attempts had been made to detect a cellulose in latex without success, but there was great difficulty in proving the presence of such a component in minute amount.

In conclusion it was suggested that, to make comparable the results of the fractionation of rubber, it was necessary to treat latex and rubber in the same manner. If, for instance, the "latex rubber" and the "dried-fresh-latex films" had been subjected to milling before fractionation, the results would have been comparable with each other and with the "crepe". The authors were well aware of the effect of mechanical treatment, and referred to avoidance of such when exposing rubber to the action of the solvent mixture, but the mechanical treatment in preparation, as it affected the coarser structure, was equally important with respect to its influence on the physical properties.

Bloomfield and Farmer stated they feared there had been some misunderstanding, both of their aims in fractionating rubber and of their experimental results. The fractionation of rubber presented a twofold problem, that of finding a theoretically sound and practically workable method of resolving a mixture of high-molecular, polymer-homologous hydrocarbons into fractions of approximately similar chain-lengths, and that of surmounting the difficulty arising from the fact that natural rubber was, by reason of its association with a proportion of nonrubber material (largely protein), not a pure hydrocarbon. The desirable objective was to fractionate pure rubber hydrocarbon and, hence, the obvious course was to eliminate all nonhydrocarbon material from natural rubber before proceeding with fractionation. Unfortunately the attainment of even imperfectly complete purification from nonhydrocarbon components involved such vigorous treatment of the rubber with reagents that maintenance of the integrity of the original carbon chains was in doubt, especially in view of recent assertions with regard to the facility with which high-molecular carbon chains could undergo scission under mechanical stress, or (in case of unsaturated substances) by the action of small amounts of oxygen. The next best thing was to purify the



hydrocarbon as far as seemed safe without risking carbon-chain scission, and especially to endeavor to free, by hydrolysis, all hydrocarbon molecules which were linked singly or in groups to nonhydrocarbon molecules (especially to protein) or joined together by hydrolyzable hetero groups. But in view of the possibility that some carbon-chain scission might conceivably have occurred, it seemed desirable to carry out parallel fractionations with less purified rubbers, first, as a safeguard (to be able to compare the molecular sizes and bulks of corresponding fractions) and, second, to determine whether, for practical purposes, the molecularly-graded fractions of crepe rubber could be substituted for the more laboriously acquired fractions of carefully purified rubber hydrocarbon.

The only way in which the "structure" of rubber could affect the fractionation of rubber hydrocarbon would be by delaying the dissolution of a proportion of molecules of each fraction, so that these ultimately turned up in the wrong fractions. This might well occur in a rapid and not very scrupulously regulated series of operations. Their procedure was designed to obviate this (the time taken for a complete fractionation of rubber was 5 months), and they believed that there was no serious disturbance from this cause. But this possibility was not to be confused with the quite different one arising from the fact that, in an impure rubber hydrocarbon, some of the molecules were apparently not just hydrocarbon molecules, but the hydrocarbon chains might be linked by or linked to heteroatoms or molecules, forming quite distinct entities with distinctive solubilities. This contingency affected to some extent acetone-extracted crepe rubber, but to a much larger extent dried latex film. The former contained only 1.8 per cent of material which was quite insoluble in benzene containing a little methyl alcohol, whereas the latter contained 27 per cent insoluble in the same mixture. Unfortunately this figure of 27 per cent, *i.e.*, three-quarters of the portion labelled "residue, undissolved", in Table III, the remainder being "high" fraction, had not been determined when their paper appeared in proof. This insoluble material from dried latex film contained no less than 1.5 per cent of nitrogen, and was being closely examined as to the nature of the protein, the character of the rubber and, if possible, the nature of the links between the two; doubtless, however, a proportion of the protein came directly from the serum and had not, since extrusion of the latex from the tree, been linked or directly associated with hydrocarbon molecules. It followed, of course, that if in a proportion of the crude rubber molecules the hydrocarbon chains were linked chemically to protein or other nonhydrocarbon material by hydrolyzable bonds (and it was to be borne in mind that it seemed to be quite possible to free rubber hydrocarbon from all but the smallest traces of nitrogenous material by hydrolysis) then the hydrolyzed hydrocarbon component ought to contain hydroxyl or possibly amino or mercaptan groups. With a view to detecting and estimating such groups in minute proportions, efforts had continuously been made, since their work on the fractionation of rubber was begun, to improve greatly the reliability and sensitivity of existing methods of determining active hydrogen, as an alternative to employ the careful but exceedingly laborious and indirect method of Midgley, Henne and Renoll for determining the total oxygen content of rubbers by combustion.

Of the other fractions of the various rubbers, it could be said:

1. They were all soluble in organic solvents.
2. They contained only small proportions of nitrogenous, or so far as could be detected, other nonhydrocarbon materials, although the small proportion of



residual nitrogen and hence the proportion of molecules not consisting entirely of homogeneous hydrocarbon increased, as would be expected with decreasing solubility of the fractions in petroleum.

3. The soluble hydrocarbon fractions from purified latex rubber and crepe rubber had closely comparable molecular weights. Those from dried latex film had not been determined.

4. The fractionation process was easily reproducible, giving consistent results.

The writers would like to point out that the "high" or No. 4 fraction of purified latex rubber (21.5 per cent) was larger than the insoluble residue (0.0 per cent, and therefore unrecorded), and not smaller, as Stevens had apparently gathered from Table II.

There was, however, one unexpected feature; the weight percentages of the corresponding fractions of dissolvable material from the three types of rubber departed materially from equality. The reason for this was not at present clear, but there was at the moment insufficient evidence to conclude that the differences arose from scission of carbon chains by mechanical stresses. Apart from this possibility there remained the adverse effect of structure on fractionation as envisaged by Stevens, and the perhaps more serious possibility that the hydrocarbon molecules might have become to some extent altered chemically (intercondensed or polymerized), as a result of the processes to which the crude rubber had been subjected. The treatment advocated by Stevens in his last paragraph might conceivably have a definite effect in disintegrating the highly nitrogenous insoluble fractions from crepe rubber and dried latex film, the exact character of which was not yet known; but it did not seem likely that, short of chemically damaging the hydrocarbon, it would bring about any serious redistribution of the only slightly nitrogenous material of the No. 2 and No. 3 fractions of crepe rubber, or the corresponding fractions of dried latex film. Furthermore, it did not seem unreasonable to expect that any protective effect of the undispersed nonhydrocarbon sheaths, as suggested by Stevens, would be overcome in a suitably-conducted, long-continued extraction with a solvent. On the other hand, their experience of the ease with which readily soluble specimens of rubber hydrocarbon could speedily become quite insoluble, presumably by cross-linking, under conditions the significant features of which were not thoroughly understood, made the spontaneous chemical modification of some part of the rubber hydrocarbon, leading to some degree of insolubilization, a source of error always to be feared.

H. P. Stevens wrote that Bloomfield and Farmer's reply treated some new aspects of this interesting but complex subject. He would therefore confine himself rigidly to the subject matter of his first observations.

Regarding the figure 21.5 per cent, this, it was explained, represented the "high" fraction, and not the undissolved residue, which was stated to be nil. It was suggested that he had misinterpreted Table II. Actually he had not quoted from, or made any use of the figures given in Table II. He had quoted only from the letterpress on the previous page (76), which stated that "the undissolved residue amounted to just over 20 per cent of the whole." The basis of his argument was a comparison of this amount of "just over 20 per cent" with the corresponding figures of 1.8 per cent for crepe rubber and 36 per cent for air-dried latex films. If the undissolved residue be nil, as is now stated, and not "just over 20 per cent", it does not invalidate the explanation he had put forward, *viz.*, that the proportion of insoluble residue was a function of the macrostructure of the rubber. It merely implied that the repeated centrifuging and other

treatment in the process of purifying latex was so drastic that the sheaths surrounding the hydrocarbon particles were substantially eliminated.

Another observation, reported many years ago, had a bearing on the matter of structure. If latex were coagulated in the presence of tannin, creping of the coagulum was insufficient to break up the integuments of the latex particles, presumably, owing to the reaction between the tannin and the protein comprising the particle sheaths. Dry crepe made in this way swelled in a solvent like smoked sheet, and the hydrocarbon diffused only slowly in the supernatant solvent. Bloomfield and Farmer appeared to favor strongly the hypothesis that the undissolved fraction derived its insolubility from the presence of a chemical combination of hydrocarbon with a nitrogenous or other complex. It was possible, although it seemed improbable that such complex molecules were present in rubber. It was also agreed that the insoluble fraction was rendered soluble by mechanical treatment as in the creping of a normal coagulum. It was more probable that the comparatively mild creping process broke up the microscopic honeycomb structure, freeing the particles of hydrocarbon, than that it broke up complex hydrocarbon-protein molecules, however large they might be. It was not a question of temperature, for moderate heating of a coagulum did not break up the protein sheaths. At least it was a fact that the honeycomb structure of an ordinary coagulum existed, for it could be seen under the microscope, and that creping broke it up. As this sufficed to explain the presence or absence of an insoluble fraction, it would appear that the introduction of the further complication of hydrocarbon-protein molecules in explanation of the phenomenon was redundant.

Bloomfield and Farmer also stated that the protective effect of the undispersed nonhydrocarbon sheaths would be overcome by a "suitably conducted, long-continued extraction with a solvent." This was unnecessarily vague. If "suitably-conducted" comprised free exposure to light and air, then the protective effect would, as they suggested, be overcome. But if those agencies were excluded, a state of equilibrium would soon be reached which would not change. He still had one or two well-stoppered flasks containing swollen pieces of smoked sheet in an excess of benzene which had been kept in a dark cupboard and had not altered for 25 years. They dated back to his first work on this subject.<sup>2</sup>

Bloomfield and Farmer replied that the cause of Stevens' misinterpretation of the figures appeared to be the distinction drawn between "insoluble residue" and "undissolved residue", the first meaning that the residue could not be dissolved because it was definitely insoluble in petroleum-acetone mixtures or in petroleum (or, as the event showed, even in petroleum-methyl alcohol), and the second merely that it had remained undissolved in the petroleum-richest mixture of petroleum-acetone which up to that point had been used as solvent, although probably soluble in whole or in part in mixtures still richer in petroleum. The figures showed that there was an insoluble residue from crepe rubber (1.8 per cent), but none from latex rubber, so that the comparable figures, for the purpose of Stevens' argument, appear to be 1.8 per cent and 0 per cent for the insoluble fractions of crepe and latex-rubber, respectively; and 12.3 per cent and 21.5 per cent for the corresponding No. 4 and "high" fractions extracted by petroleum-acetone mixtures containing 64 per cent and upwards of petroleum. The figures for air-dried latex film were not included in the original draft of the paper, but were added in proof as an appendix, principally for the purpose of contrasting the writers' experience of the degree of solubility of fresh latex-film with the surprising statement of Kemp and Peters, then just published,

respecting the small degree of solubility of films from freshly-imported ammonia-preserved latex. The fractions Nos. 1-4 were not actually differentiated in Table III, but the same ranges of solvent composition applicable to those fractions in crepe and latex rubber applied here also.

With regard to the contention about the existence of an important connection between fractionation percentages and the "structure" of crude rubber, it was clear that the degree of its soundness would be a measure of the lack of success in carrying out a true fractionation of the hydrocarbon in crepe rubber, in spite of the precautions for avoiding, or so far as possible obviating, all factors except solubility. The fact that the fractions, especially those from crepe-rubber, contained nitrogen, and possibly traces of oxygen, showed that the fractionation, considered as a fractionation of rubber hydrocarbon, was imperfect, but the writers could not see that the comparative results for crepe and latex rubber supported in any serious way his contention.

The writers could not but regard Stevens' reliance on his observation with smoked sheet as unfortunate for the purpose of his argument. Existing evidence pointed to the hydrocarbon of this variety of rubber being in some serious degree altered by the process of its preparation, the alteration producing insolubility. For this reason smoked sheet was excluded from the fractionation experiments. The writers would especially stress the observations of Spence and Ferry<sup>3</sup> as to the marked insolubilizing effect of smoke on rubber hydrocarbon; furthermore, the general observations of these authors concerning the ease with which rubber hydrocarbon could be sufficiently altered to render it in large measure less soluble agreed with many of the writers' observations, and that possibility of error by actually producing insolubility in some part of the hydrocarbon had been as much of a bugbear as the opposite one of producing solubility by the degradation action of traces of oxygen under the influence of light.

Finally with regard to the nature of the association of protein with rubber hydrocarbon, there was good reason to believe that the large bulk of the protein was not connected by chemical links to the hydrocarbon, since it could be effectively removed by repeated centrifuging or by repeated creaming with agents which did not appear to owe their effectiveness in any degree to their basic or acidic hydrolyzing capacity. Hence a substantial part of the residual nitrogen in the fractions might well represent uncombined protein. There was, however, a small residual nitrogenous content of the rubber which was so retentively held as to suggest that it might be chemically linked to the rubber. The nature of this association as indicated above was at present being investigated, and the writers could not prejudge the issue. If, however, even a very small proportion of protein were linked to rubber hydrocarbon by oxygen, nitrogen or sulfur links, this might go a long way in the direction of linking together hydrocarbon chains.

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<sup>2</sup> Stevens, *India-Rubber J.* **46**, 345 (1913); *Kolloid-Z.* **14**, 91 (1914).

<sup>3</sup> Spence and Ferry, *J. Soc. Chem. Ind.* **58**, 345 (1939).

# ELASTIC AND THERMOELASTIC PROPERTIES OF RUBBERLIKE MATERIALS

## A STATISTICAL THEORY \*

EUGENE GUTH

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and

HUBERT M. JAMES

PURDUE UNIVERSITY, LAFAYETTE, IND.

A statistical theory of the elasticity of rubber and similar high-molecular compounds was proposed by one of the authors several years ago<sup>9</sup>, and an extended form of the theory was presented recently<sup>10</sup>. The theory is applied here to vulcanizates, and shows the dependence of stress on both temperature and deformation for both extension and compression. The foundations of the theory will be stated precisely, inasmuch as some recent articles dealing with it are likely to lead to misunderstandings concerning the assumption of free rotation and structure of long-chain compounds, such as vulcanized rubber.

The possible rôle of kinetic effects for the rubber type of elasticity has been discussed qualitatively by Wöhlisch<sup>28</sup>, Busse<sup>4</sup>, Karrer<sup>14</sup>, Meyer, Susich and Valkó<sup>18</sup>, and Shacklock<sup>21</sup>. The first quantitative theory was developed by one of the authors in 1934 and published later, partly in collaboration with Mark<sup>9</sup>.

In the statistical theory, the main assumption is that of quasi-free rotation in a rubber molecule around a single carbon-carbon bond. An important consequence of this free rotation is that the molecules are coiled in the unstretched state. The contraction of stretched rubber is due mainly to the tendency of the stretched chain to change from a less probable stretched form back to the most probable coiled form. This happens in accordance with the statistical interpretation of the second law of thermodynamics, and is not caused by forces. Our theory, then, is that the kinetic motion of freely rotating groups in the rubber molecule is the main cause of contraction.

According to this theory, stretched rubber shortens when heated because the kinetic energy increases, and therefore the tendency of a rubber molecule to go back to its most probable curved form is increased. The other anomalous thermoelastic properties of rubber—namely, that it becomes warm when stretched adiabatically and that its coefficient of linear thermal expansion is negative—can be derived from the first mentioned fact by thermodynamic considerations.

Some of the older theories of rubber elasticity—for instance, those of Fikentscher and Mark<sup>5</sup> and of Mack<sup>15</sup>—are based entirely on forces operating between and in the rubber molecules. These can be compared with such a theory of a real gas, which recognizes only the forces and neglects the kinetic energy, *i. e.*, uses the equation:

$$p = -a/v^2$$

without taking into account the kinetic term  $RT/(v-b)$ . On the other hand, in the statistical theory these forces too are recognized. They have an influence

\* Reprinted from *Industrial and Engineering Chemistry*, Vol. 33, No. 5, pages 624-629, May 1941.

during crystallization and at the highest elongations shortly before breaking.

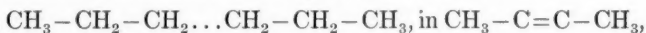
The experimental evidence concerning the dependence of the stress on both temperature and extension supports the theory. On the other hand, apparent contradictions—for instance, stress-strain curves showing a decreasing stress with increasing temperature at a constant elongation—are due to the failure to attain equilibrium conditions and other disturbing but secondary factors.

#### QUASI-FREE ROTATION IN THE RUBBER "MOLECULE"

Quantum mechanical treatment as well as experiment shows that there can be free rotation around a single carbon-carbon bond. On the other hand, theory and experiment agree that a double carbon bond is rigid, and defines a certain plane which is characteristic of the molecule containing a double bond.

We wish to elaborate the concept of free rotation when a molecule possesses different configurations (stable arrangements) of equal relative probability. The configurations might be separated by energy barriers so that a free rotation in the old sense might not be possible. It should be emphasized that the concept of free rotation, as introduced in organic chemistry, does not suppose more than the existence of such a quasi-free rotation. The only assumption necessary is that the energy barriers should not be too high, for then a relative equilibrium of the different relative configurations may take place in a short time. For brevity the term "free rotation" will be used in the following discussion to mean quasi-free rotation, except where the contrary is explicitly stated.

There is little doubt about the existence of quasi-free rotation around a single bond in an unbranched unsaturated hydrocarbon chain:



or in isoprene  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$ , and, therefore, in a rubber molecule consisting of a large number of isoprene groups.

The possibility of free rotation in a solid might appear strange, until it is remembered that, during the last decade, many solid bodies were found to exhibit more or less free rotation of their molecules as a whole or of groups of their molecules, like sodium chloride. Furthermore, it can be shown theoretically that, in a network formed by chains interlinked by cross bonds, the free rotation persists.

#### STRUCTURE OF ELASTIC LONG-CHAIN COMPOUNDS

The most characteristic property of vulcanized rubber is the comparative absence of permanent set. If we accept the fact that crude rubber has a long-chain structure, it follows directly that vulcanizing must lead to a strengthening of the cross-bonds already present in crude rubber, simultaneously with the introduction of new cross-bonds. For only cross-bonds hindering the gliding of the molecules on each other can completely suppress plasticity—*i. e.*, permanent set.

By cross-bonds we mean primary and secondary (van der Waals forces) bonds. It is then clear that all theories concerning vulcanization are special cases of general cross-bond formation as stated before. For the theory according to which vulcanization consists mainly of the formation of intermolecular sulfur bridges, this is obvious. However, it applies also to the theory according to which vulcanization consists in further polymerization of rubber molecules under the catalytic influence of sulfur, because a lengthening of the chains increases the interaction per pair of chains and, therefore, resistance to gliding.

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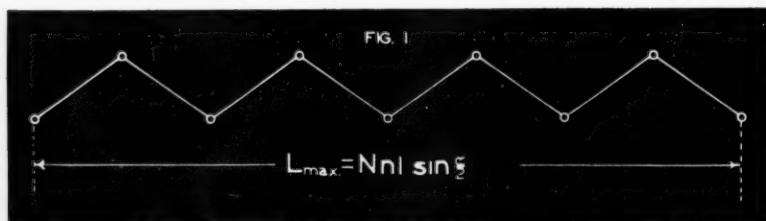
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kind of three-dimensional network was put forward by Hock<sup>12</sup> and by Meyer and Mark<sup>16</sup>. Subsequently many authors—for instance, Boggs and Blake<sup>1</sup> and Garvey<sup>8</sup>—discussed the rôle of sulfur in vulcanization. The most recent reports are by Williams<sup>27</sup>, Brown and Hauser<sup>3</sup>, and Fisher<sup>6</sup>. Their discussions are concerned with whether all or part of the sulfur forms bridges, and whether there is a relation between physical properties and the proportion of combined sulfur. In the present work, however, it is not important whether all or part of the sulfur forms bridges or real bridges exist. Only strong interaction between the chains is postulated, which is strengthened by curing. This is the simplest interpretation of experimental facts, regardless of whether or not chemical bridges are assumed.

According to the present picture, both vulcanized and crude rubber consist of long-chain molecules interlinked by cross-bonds to a three-dimensional network. The difference between vulcanized rubber and crude rubber is quantitative.

There are more and stronger cross-bonds in vulcanized rubber than in crude rubber. Consequently, vulcanized rubber is less plastic than crude rubber. The intermolecular Brownian motion of translatory character—*i. e.*, the translation of the molecules as a whole—is completely hindered. Crude rubber, on the



other hand, exhibits a less defined network, and some intermolecular Brownian motion is still possible. Only in case of deformations whose duration is short compared with the relaxation time of this intermolecular Brownian motion does the network behave as if it were perfectly defined. Deformations of short duration imply small deformations. However, an approximately defined network leading to approximately perfect elasticity is to be expected also for larger elongations if they are executed quickly enough.

This general picture of the network structure of vulcanized rubber is all that is needed for the theory developed here. This theory is the first approximation to the actual case. A network is necessary to have true elasticity, because a stress applied to a microscopic piece of rubber can stretch the individual chain-molecules only if the chains are linked together in some way. Two models for rubber-like solids will be discussed in the following sections.

#### SIMPLEST MODEL FOR RUBBERLIKE ELASTICITY

The simplest model was treated previously<sup>9</sup>, and will be discussed here only briefly. The model consists of  $M$  parallel strings running through the whole of a certain piece of rubber,  $M$  being the number of strings per unit cross-section. Each string consists of  $N$  molecules, and each of the molecules contains  $n$  freely rotating bonds. For the case of a normal hydrocarbon chain molecule:  $\text{CH}_3 - \text{CH}_2 - \dots - \text{CH}_2 - \text{CH}_3$ ,  $n$  is of the order of 100 to 10,000. Such a molecule is simpler than the rubber molecule because there are no double bonds and no

methyl groups. In this model the interaction between the chains which actually gives rise to a finite incompressible volume is neglected.

According to stereochemistry, the distance,  $l$ , between two neighboring carbon atoms is 1.54 Å. U., and the angle,  $\alpha$ , between the two valence bonds is about  $109^\circ$  C. When we stretch the chain to its maximum length, the distance between the end groups is given by:

$$L_{\max.} = Nnl \sin \frac{\alpha}{2} \quad (1)$$

We may readily see that this maximum length of string can be obtained in only one way—*viz.*, when all bonds are located in one plane and form a zigzag line (Figure 1). As a result of free rotation, however, the length of the string between the two end-groups may have various values intermediate between zero and this maximum value. Each of these lengths can be materialized in several ways, and represents a configuration, or a state of the string, of different probability. Obviously, then, it is necessary to define statistically the length of each string which is composed of many parts, for free rotation is so rapid that only average values can be observed experimentally. Needless to say, this statistical length is not the same as the maximum length defined above, but is shorter. The reason is evident if it is considered that, when a flexible string is thrown into the air, it falls to the ground twisted or kinked in some fashion rather than in a straight line.

The probability function,  $W$ , which represents the probability that the string composed of  $N \times n$  freely rotatable bonds with valence angle  $\alpha$  has a given total "length" (distance from one end of the string to the other end), is, for small enough length:

$$W(nN, l, \alpha; L) dL = A e^{-\beta L^2} L^2 dL \quad (2)$$

where

$$\beta = 3/2nl_a^2$$

$$l_a = l \cot \alpha/2$$

Equation 2 shows that an average distance exists between the chain ends—*viz.*, the value  $\sqrt{\bar{L}^2}$  for which the function  $W$  reaches its maximum value. This average distance is given by:

$$\sqrt{\bar{L}^2} = l_a \sqrt{\frac{2}{3}} \sqrt{nN} \quad (3)$$

*i. e.*, this average distance is proportional to the square root of the number of links of the string, as might be expected from the statistical character of the whole calculation. (It should be emphasized that Equations 1 and 3 might not be combined to calculate the maximum possible percentage elongation of this molecular model. If we want to make a rough estimate, we must put  $N=1$  into both Equations 1 and 3.)

From this probability function, the entropy of the string can be calculated according to Boltzmann's principle:

$$S = k \log W' \quad (4)$$

where we replace  $W$  with  $W'$ , the probability function for the projection of the "length" on the direction of the stress. From the entropy, the equation of state can be obtained in exactly the same way as the one by which we obtain the equation of state of an ideal gas. The result is:

$$Z = (2kT/Nnl_a^2)L$$

To obtain the stress for  $M$  parallel strings, we have to multiply this value by  $M$ :

$$Z = (M2kT/Nnl_e^2)L \quad (5)$$

This model explains the anomalous thermoelastic behavior of rubber, according to which the length  $L$  at a given stress  $Z$  decreases with increasing temperature  $T$ .

According to the above theoretical stress-strain equation, the length will be equal to zero when the stress becomes zero. This is not correct, because it would mean that the rubber has a zero volume in the unstretched state.

The bundle model of ideal rubber is not isotropic, since it is extensible only in the direction of the strings which form the bundle. However, Fowler showed that Equation 5 holds also for a spatial model consisting of a cubic array of molecules, each edge of a cube consisting of a molecule with freely rotating bonds. It turns out that the cross-connections of a certain type do not affect the stress at a given length. This holds only for a symmetrical type of cross-bond. This is significant because it shows that a consistent spatial model can be set up in which cross-bonds exist, which, however, do not restrict the free rotation necessary for obtaining the equation of state given above.

#### MODEL FOR INCOMPRESSIBLE RUBBER

In the second model the interaction between the chains is taken into consideration, assuming incompressibility. In the simple model, only the length of the stretched rubber was considered. This implied that stretching in one direction does not affect the dimensions of the piece perpendicular to the direction of stress. We know, however, that vulcanized rubber is incompressible up to 300 per cent elongation<sup>13</sup>. Furthermore, it was not taken into account that the volume of rubber in the unstretched state is determined mainly by the interaction between chain-molecules. The possibility that groups of inactive molecules are present in the network was not considered either.

As a model for rubberlike solids similar to vulcanized soft rubber compounds, we assume a network consisting of randomly distributed chains connected by cross-bonds. These chains will interact with one another and with aggregates of inert molecules which are only weakly connected with the network or not connected at all. These groups of inactive molecules may have more or less mobility within the network, and can change their relations to other chains if the rubber is stressed. The interaction of the chains constituting the network with each other and with the inert molecules leads to a finite volume of the rubber which is subject to external forces. There will be an internal pressure of an approximately hydrostatic character because of the possibility of rearrangement of the internal strains by motion of the inert agglomerates which are only loosely connected with the network. Our model assumes a network stretched across an incompressible fluid.

We consider a cubic centimeter of rubber. After a stretch applied in the  $x$  direction, its dimensions will be  $L_x, L_y, L_z$ . Here  $L_y = L_z$ , because decrease in breadth takes place in the same way in both directions perpendicular to the stress. The incompressibility, meaning that the volume of the rubber has the same value after stress as it had before, leads to the equation:

$$L_x L_y L_z = 1$$

or, because  $L_y = L_z$ :

$$L_x L_y^2 = 1$$

The probability,  $W$ , that the stretched piece of rubber has a length  $L_x$  in the  $x$  direction,  $L_y$  in the  $y$  direction, and  $L_z$  in the  $z$  direction, is given by:

$$W dL_x dL_y dL_z = A e^{-\beta(Lx^2 + Ly^2 + Lz^2)} dL_x dL_y dL_z \quad (6)$$

or taking into account the relations given above:

$$W dL_x dL_y dL_z = A e^{-\beta(Lx^2 + 2/Lx)} dL_x dL_y dL_z \quad (6A)$$

Using Boltzmann's principle again, we obtain the equation of state:

$$Z = M2\beta kT (L_x - 1/L_x^2) \quad (7)$$

At constant temperature, Equation 7 gives an isothermal stress-strain curve:

$$Z = \text{constant} (L_x - 1/L_x^2)$$

i. e., a change of the scale of the ordinate axis should make all  $Z(L)$  curves similar to the curve:

$$(L_x - 1/L_x^2)$$

The slope of  $Z = Z(L_x)$  at  $L_x = 1$  (unstretched state) is three times the slope of the asymptote to that curve at high values of  $L$ .

For Young's modulus, Equation 7 yields:

$$E_1 = dZ/dL_x = M2\beta kT (1 + 2/L_x^2) \quad (8)$$

i. e., this modulus has at the start a constant value three times as high as the constant value which it approaches for large  $L_x$ .

Referring the stress to the actual cross-section, an alternative Young's modulus results:

$$\begin{aligned} \zeta &= Z/L_y^2 = L_x Z \\ E_2 &= d\zeta/dL_x = L_x \cdot dZ/dL_x + Z \end{aligned} \quad (9)$$

All the foregoing formulas hold not only for stress ( $L > 1$ ), but also for unilateral compression ( $L < 1$ ).

**Conclusions.**—The model yields automatically a negative linear thermal expansion coefficient in the direction of the stress and a positive one perpendicular to that direction.

The model can be extended to describe a compressible material, both for the unstretched and the stretched cases.

For higher elongations (above 300-400 per cent), the deviations from Formula 2 for  $W$  have to be taken into account. The general formula is given by:

$$W(nN, l; L) = \frac{2LdL}{l^2\pi} \int_0^\infty \left( \frac{\sin lu}{lu} \right)^{nN} (lu) \sin(Lu) d(lu) \quad (10)$$

This expression can be expanded into a series, with Formula 2 as the first term if we expand  $(\sin lu/lu)^{nN}$  and then carry out the integration of the series term by term. These deviations are descriptive of those conditions which are partly responsible for the stiffening of rubber at higher elongations. It should be emphasized that Expression 10 may be derived on essentially the same assumption as Expression 2.

Curving of chains due to thermal fluctuations of the magnitude of the  $n$  or  $Nn$  valence angles has not been included. This effect, which can be neglected to the first approximation for the solid state, might play a rôle in determining the shape of long-chain molecules in solution. It can occur without the presence of free rotation, and has to be distinguished from curving due to free rotation. This was not considered in older kinetic theories of rubber elasticity.

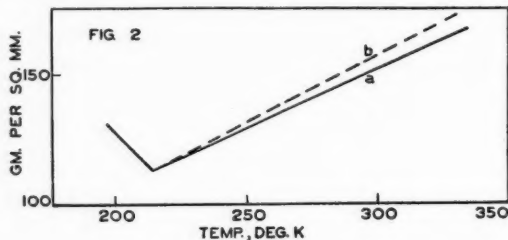
Effects of the same type, but different in origin, can play a rôle at the highest elongations just before the breaking point—*viz.*, a deformation of the valence angles after the chains are stretched to their maximum zigzag length (compare Figure 1) and a stretching of the main valence bonds after the valence angles are stretched to the maximum value  $\pi$ . In addition, mostly crystallization phenomena are superimposed on these effects.

Time effects, *i. e.*, the relaxation times, may be incorporated into the statistical theory of rubber elasticity.

Strong hindrance of free rotation makes  $W$  dependent on temperature, and destroys the simple proportionality between stress and  $T$  at a constant elongation. At the same time a more temperature-dependent internal energy can also be present.

#### EXPERIMENTAL EVIDENCE FOR THE STATISTICAL THEORY

For testing the theory, only truly reversible stress-strain-temperature curves which show no appreciable hysteresis can be used. Not much material in the literature can be used for this purpose. In addition, we cannot expect that all kinds of rubber compounds which show a great difference in physical properties will behave according to the simple model discussed in the foregoing section.



*Stress-temperature curves at constant elongation.*—These curves are referred to as isometrical curves, or isometrics for short. At constant elongation, Equation 7 predicts a proportionality between stress and absolute temperature. Measurements of Meyer and Ferri<sup>16</sup> on a vulcanized rubber-sulfur compound (their Sample 1) confirm this at 350 per cent elongation (compare Figure 2). Curve *a* is uncorrected for temperature expansion and curve *b* is corrected for temperature expansion. Curves showing a linear dependency of stress on temperature have been observed at Notre Dame by Anthony and Caston for different vulcanized pure gum compounds..

From isothermals given by Ornstein, Eymers, and Wouda<sup>20</sup>, approximately linear  $Z$ - $T$  curves can be deduced too. A linear  $Z$ - $T$  curve means physically that there is, in addition to the contribution of thermal agitation (entropy elasticity), a contribution from forces (force elasticity) leading to an internal energy,  $U$ , which depends on the elongation alone but not on the temperature:

$$Z(L, T) = a(L) + b(L)T = \left( \frac{\partial U}{\partial L} \right)_T - \left( \frac{\partial S}{\partial L} \right)_T T \quad (11)$$

This is the most general equation of state for which  $U = U(L)$  and  $S = S(L)$  are both functions of  $L$  alone. That  $b(L) > 0$  below 400 per cent elongation is shown by the work of Wiegand and Snyder<sup>26</sup> on stationers' bands. They find  $a(L)$  decreasing with increasing elongation and going through zero to negative



values. Near the elongation for which  $b(L)=0$ ,  $Z(L,T)$  should show proportionality with  $T$ . However, according to Vogt<sup>23</sup>, the latter authors find a decrease of modulus with  $T$ . Furthermore, their stress-strain curves are probably adiabatic rather than isothermal.

Qualitative evidence for the existence of entropy elasticity is contained in a number of older papers dealing with the temperature dependency of the modulus, the contraction of stretched rubber on heating, and change in temperature of rubber when stretched adiabatically<sup>25</sup>.

*Dependence of specific heat at constant elongation on elongation (caloric equation of state).*—It can be shown thermodynamically that an equation of state of the following form:

$$Z(L,T)=a(L)+b(L)T \quad (11)$$

leads to the fact that the specific heat at constant elongation  $C_L(L,T)$  is independent of the elongation, and depends on the temperature only:

$$\partial C_L / \partial L = 0 \quad (12)$$

Conversely, if Equation 12 is valid, the equation of state has to be of the form of 11.

Ornstein *et al.*<sup>20</sup>, using the same rubber stock for which a linear equation of state similar to Expression 11 can be derived, obtained a strong dependence of  $C_L$  on  $L$ . Unpublished work of collaborators of one of the authors made it plausible, however, that Ornstein *et al.* measured some secondary effects rather than  $C_L$  as a function of  $L$  and that really  $\partial C_L / \partial L = 0$  is to be expected. Recently Boissonas<sup>2</sup> published measurements on a pure gum stock which also shows no variation of  $C_L$  with elongation. He does not mention, however, the connection between  $\partial C_L / \partial L$  and the equation of state.

This is about all the material that can be used at present to test the dependence of stress on temperature at constant elongation.

*Isothermals (stress-strain at constant temperature).*—According to Equation 7, the dependence of stress on temperature should be given by:

$$Z(L,T) = \text{constant} (L - 1/L^2)$$

where  $L$  denotes the relative length.

The only stress-strain curves which can be used for testing Equation 7 are those given by Meyer and Ferri<sup>16</sup> for the same rubber-sulfur stock which showed proportionality of the stress with the absolute temperature at constant elongation.

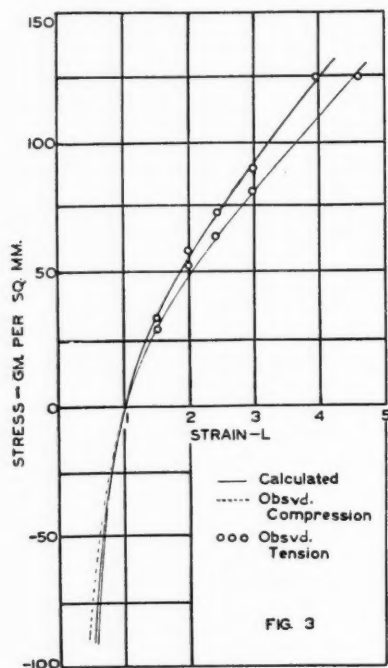
In Figure 3 the circles are the experimental points, the full line is the theoretical curve. The agreement is remarkable, inasmuch as the theoretical equation does not contain any arbitrary constants except a scale factor. This scale factor is reducible to molecular constants,  $(2/Nn\lambda_a^2)MkT$ .

A stress-strain curve for a loaded stock (25 per cent carbon black) observed by Shacklock<sup>21</sup> also agrees well with the theoretical curve, as shown in Figure 4. A stress-strain relation whose first two terms are identical with Equation 7 was given by Shacklock<sup>21</sup>. His complete expression, however, which is much more complicated than Equation 7, cannot be considered as consistently derived. Fisher and Gerke<sup>7</sup> pointed out that "the fundamental basis for this model does not appear to have been sufficiently developed with respect to the properties of long-chain molecules to render possible a searching test of its validity or a quantitative test with respect to energy relations".

It should be pointed out that we can obtain from the above constant in Equation 7 a "molecular weight" of rubberlike solids, defined as the weight of the chain between two junctions of the network.

In Figure 3, the negative branch ( $L < 1$ ) of  $Z(L)$  refers to compression. The extension and compression branches form continuous curves. The whole stress-strain curve satisfies the following conditions of Sheppard and Clapson<sup>22</sup> as quoted by Vogt<sup>24</sup>. (1) The curve passes through the origin, with negative curvature (convex upward). (2) The compression branch passes downward, with rapidly increasing slope, and must have a vertical line of 100 per cent compression as its asymptote. This was found experimentally to be true.

The assertion of Sheppard and Clapson<sup>22</sup> that, even in case of a continuity of the extension and compression branches, the two cannot be considered as represented by one, and that it is not possible to extrapolate one from the other does



not hold for our Equation 7. According to this equation, extension and compression curves are really one curve. (The compression curve was drawn so that the extension branch fits Meyer and Ferri's stress-strain curve.)

The theoretical compression curve of Figure 3 agrees with experimental data of Sheppard and Clapson (dashed curve) fairly well. This agreement could be improved by using another scale factor, since Meyer and Ferri<sup>16</sup> and Sheppard and Clapson<sup>22</sup> used different materials. A closer comparison cannot be made because Sheppard and Clapson did not investigate the temperature dependence of their data.

Interesting equations for finite extensions and compressions were developed by Hencky<sup>11</sup> and Mooney<sup>19</sup>, using the continuity theory of elasticity. Their equations, however, are more complicated than ours, and do not show the temperature dependence. Furthermore, it is questionable whether they can be derived from molecular considerations.

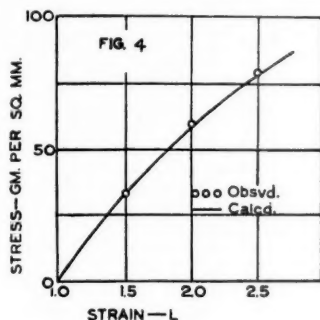
This paper stresses the importance of a statistical effect as the main cause of



the retracting force. It does not mean, however, that the intra- and intermolecular forces are to be neglected. On the contrary, the theory of rubber elasticity is developed here from fundamental concepts similar to those used in the molecular explanation of the properties of normal solids in statistical mechanics.

*Apparent contradictions of the statistical theory.*—Mention should be made of the older papers of Bouasse, of Somerville and collaborators, and of van Rossem and van der Meijden, which are treated by Vogt<sup>23, 24</sup>. According to these investigators, modulus decreases with increasing temperature. However, in these cases (with the exception of Bouasse), first-extension stress-strain curves were taken and no equilibrium was reached. There are no truly reversible equilibrium isothermals or isometrics known which show a decrease of modulus or stress with temperature. On the other hand, all known truly reversible equilibrium data support the statistical theory. Needless to say, more precise experimental material is urgently needed.

A detailed discussion of the extended statistical model of rubber, with a number of applications not mentioned here, will be published elsewhere.



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# RUBBER PHOTOGELS \*

HENRY P. STEVENS

When a rubber sol is exposed to light in an air-tight vessel, it sooner or later gels, provided the concentration of the rubber is not too low and the air space above the surface of the sol is not too large.

The first published observation of the gelling of a rubber sol in light was made by Porritt<sup>1</sup>. Finding that the exposure of a rubber sol containing sulfur did not induce vulcanization, he repeated the experiment with the removal of oxygen, providing also a control tube without sulfur. Nothing happened with the tube containing the sulfur, but the control tube "after a few days suddenly set to a gel without any obvious preliminary increase in viscosity." This gel on exposure (to air) was found to be rapidly transformed to a liquid. From the context it seems that the solvent used was benzene, but no information is given as to the type of rubber, whether raw or milled, concentration or other details, or how the removal of air or oxygen was accomplished.

This observation of Porritt's is referred to in two or three subsequent publications by chemists who have noted similar occurrences. Thus, Smith<sup>2</sup> reported the gelling of a sol of ether soluble rubber; and Meyer and Ferri<sup>3</sup> found that, although rubber in solution is readily degraded in light and air, it polymerizes to an elastic jelly when exposed to ultraviolet light. But previous to the publications of Smith and of Meyer and Ferri, the subject had been examined in detail by Pummerer and Kehlen.<sup>4</sup> This paper seems to have been overlooked.

To distinguish rubber gels formed in this manner from other types, the author suggests the name of "photogel". When referring to the formation of such gels, authors generally emphasize the exclusion of oxygen by nitrogen or by the use of evacuated tubes. But total removal of oxygen is not necessary. The first observations here recorded were made with benzene sols which had been put in well stoppered wide-mouth glass bottles for lecture purposes, and which had been left standing on the bench against a window for many weeks. The gel was elastic but not very stiff. A portion removed soon liquefied when exposed to light and air, but remained unaffected for several weeks in darkness, either when left to itself or immersed in benzene. The vessel was loosely stoppered, providing easy access of air. On exposure to light, the lump of gel dispersed completely in a few hours. When the stopper of the original bottle of gel was taken out, the ingress of air caused the upper part of the gel to liquefy. The stopper was replaced without delay and, on further exposure to light, the liquefied gel set once more.

This experiment discloses several characteristics of photogels, in particular that evacuation is unnecessary and that enclosed air delays gelling, also that the gel liquefies in air, but not unless exposed to light. Further, that a gel which has been liquefied by exposure to air and light can be reconverted to a gel if the amount of air admitted is small. It also shows that diffused daylight is sufficient to cause gelling, although direct sunlight or a mercury vapor lamp may be more efficient. This being the case, it seems strange that the gelling effect of light with restricted access of air has not been earlier and more frequently reported. As

\* Reprinted from *Transactions of the Institution of The Rubber Industry*, Vol. 16, No. 4, pages 211-240, December 1940.

will be shown later, benzene sols gel slowly, and better results may be obtained with other solvents.

Pummerer and Kehlen<sup>4</sup> realized at an early stage of their investigations that the rate of gelling was influenced by catalysts or sensitizers. It was found that substances of a ketonic or aldehydic constitution were the most effective in promoting gelling. They used both aliphatic and aromatic ketones, but did not give data on the rate of gelling induced by these various sensitizers or the amounts required. With some, as with benzaldehyde, the results varied. In spite of their informative paper, there are many details on which information is lacking. In regard to the properties or character of the rubber resulting after the removal of solvent from the photogels, they conclude, on somewhat scanty evidence, that the rubber recovered closely resembles vulcanized rubber, and results from the coupling of several rubber molecules by carbon ridges. On this assumption and according to present day views, gelling of rubber sols arises from the linking of long thread-like molecules to form three dimensional complexes. Thus it is assumed that the insolubility of vulcanized gels results from the formation of sulfur bridges, and similarly three dimensional complexes might be expected to result from the formation of oxygen bridges. It is not proposed to discuss the theory of vulcanization or the formation of photogels at this stage. There are facts both for and against the "bridge" theory. It is, however, apparent that, whatever theory be favored, the resemblance or divergence of these photogels from natural gel rubber and from gels formed by vulcanization, particularly the old type of vulcanization with sulfur or sulfur chloride, is a matter of interest. From what follows it will be seen that photogels differ considerably from natural gels or gels formed by the action of vulcanizing reagents.

*Experimental.*—Samples of rubber solutions in benzene in stoppered bottles in front of the window had been observed from time to time to gel, the change being gradual, not sudden, as reported by Porritt<sup>1</sup>. First, a ropiness appeared, followed by a weak gel, which would not hold together when the bottle was inverted. Finally, a stiff gel formed, the surface of which vibrated when the bottle was tapped. Sometimes the gelling could be seen to begin on the wall of the vessel and always on the side exposed to light.

As stated, rubber sols in benzene gel slowly. They gel much faster in carbon tetrachloride. The purity of the solvent does not seem to affect the rate of gelling, as might have been anticipated if the rate were determined by a catalyst present in small proportion. A further improvement in rate of gelling is obtained with either of these solvents when a part is replaced by acetone, as will be seen from Table III.

For small quantities, such as half a gram, the rubber solution was sealed off in glass tubes. For larger quantities a 6 in. x 1 in. boiling tube conveniently holds 2 grams of rubber and 40 cc. of solvent, leaving about 10 cc. of air space. Flasks may also be used. When fitted with a sound cork and varnished with cellulose lacquer, these larger vessels remain gas-tight. If the air is to be removed, the cork is fitted with a piece of quill tubing, which is drawn out and sealed off after evacuation. Such vessels have been found to hold their vacuum after several months' exposure to sunlight. By evacuating and gently warming the vessel immediately after filling and before the rubber has swollen sufficiently to block the tube, the air is carried away in the current of solvent vapor. This results in complete removal of the air, as it is boiled off from the solvent as well as from the surface of the rubber and the cork. If this method of closure is employed, the amount of air remaining in a sealed vessel after this treatment

must be excessively minute. In many cases parallel experiments were made with sealed glass and stoppered vessels. For small quantities, half a gram of rubber is introduced into a 6 inch x  $\frac{5}{8}$  inch test-tube, which is then constricted about 1 inch from the mouth, 10 or 12 cc. of solvent is then introduced through the constricted part by a funnel made by drawing out a test-tube and cutting the capillary. The tube is then evacuated, and sufficient heat is applied to boil off a small quantity of the solvent when the tube is immediately sealed. Unless otherwise stated, all tubes contained 5 grams of rubber for every 100 cc. of solvent or solvent mixture.

The tubes were laid flat in boxes placed in a dark cupboard. They were taken out once a day and well shaken to obtain a uniform sol before exposing to light. This took up to a week, according to the type of rubber and solvent used. There were certain exceptions referred to below. The tubes were placed against the window in racks. The light had to penetrate the glass window and the glass of the tube, so that much of the short wave-lengths were filtered out. On sunny days the tubes were exposed to direct sunlight for only part of the day. Under these conditions, even in winter and in the presence of ketones, gelling took place in a few days or weeks. The first few series were exposed in London in November, 1938.

*Sensitizers and influences affecting rate of gelling.*—In the following year the exposures were more favorable, the tubes being placed in a window facing south in the open country. Under these conditions an evacuated tube, using a solvent mixture of two parts carbon tetrachloride and one part acetone gels in 3 to 4 hours. With more powerful sensitizers, such as benzophenone, the time of gelling is even shorter. Indeed, incipient gelling may take place in an evacuated tube before the rubber is completely dispersed unless precautions are taken to keep the tubes fully protected from diffused daylight. Although a great number of solvents and sensitizing agents have been tried, there is no medium more suitable for preparing a quantity of a photogel than a mixture of carbon tetrachloride and acetone, as both are easily removed from the resulting gel on account of their low boiling points. Gelling is always slower in pure solvents, although, given time, it invariably takes place. Solvents are placed in the following order of efficiency: carbon tetrachloride, ethylene bromide, chloroform, monochloro- and dichlorobenzene, di- and tri-chlorethylene, ethyl ether, benzene and ligroin (petroleum ether). Ethyl ether containing peroxides, or in the presence of peroxides such as barium peroxide, is efficient, and rivals any of the active sensitizers. In ligroin (b.p. 40-60°) gelling is slow, and some sealed evacuated tubes have now been exposed to sunlight for eighteen months without photogels forming. The conclusion is reached that a petroleum, free from impurities, in an evacuated tube is probably completely inert. For testing the efficiency of sensitizers, ligroin or a pure petroleum is therefore the best medium, provided it will dissolve the sensitizer; unfortunately, this is not always the case. Petroleum ether was first used by Caspari for work on rubber gels<sup>5</sup> and is preferred by Kemp and Peters in their latest publication<sup>6</sup> as the most appropriate solvent for rubber.

Ethyl ether, which has been generally used for the separation of sol and gel fractions, and was also employed by Pummerer in his work on photogels<sup>4</sup>, is unsuitable on account of the tendency to form peroxides. This may account for some want of agreement between his records and those given in this paper. Failing ligroin, the best relatively inert solvent is benzene. Some figures are given in Table V in connection with other data, from which it will be seen that a benzene sol takes some weeks to form a photogel.

Most of the comparative experiments were made with a carbon tetrachloride-acetone mixture. The presence of a little air delays gelling; consequently the proportion of air must be restricted. The greater the volume of air the longer gelling is delayed. This will be seen from Table I.

TABLE I

Experiment	(1)	(2)	(3)	(4)	(5)
Approximate air volume (per cent).....	10	20	30	40	50
Days taken to form a firm gel.....	45	50	53	67	86

The exposure was in January. The progress was very evident. (1) gelled before any of the others and was already a stiff gel when (2) was a weak gel and (3) was only slightly ropy. This latter was fully gelled before (4) and (5) began to gel. The tubes remained exposed for several months. At the end of the third month syneresis had set in, about 10 per cent of the volume of the liquor in (1) being expelled at the bottom of the tube, presumably, therefore, consisting mainly of the heavier carbon tetrachloride. There was less at the bottom of (2) and still less at the bottom of (3). (4) showed separation of liquor in small quantity both at the bottom and top and (5) hardly at all.

If a tube be exposed with free access of air, as through a capillary, gelling seldom occurs. A gel may form under these conditions, in the presence of an active sensitizer, on the side of the tube exposed, but this gradually disperses, with loss of viscosity of the whole liquid. The first effect of exposure when a limited amount of air is present is generally to reduce the viscosity, and the sol becomes mobile before a photogel begins to form. In the absence of air, as in a thoroughly evacuated tube, this initial reduction in viscosity does not always take place. The conclusion drawn is that the first effect of irradiation is the oxidation of the rubber, and not until the oxygen present is exhausted does gelling set in. The sensitizer which promotes gelling also promotes oxidation in the presence of air and, with a sufficient excess, further oxidation of the rubber ensues. In such cases the liquid becomes cloudy and frequently darkens. Examination of the products formed with free access of air has not yet been undertaken.

The rate of gelling is also influenced by the concentration of the sol, as shown in Table II.

TABLE II

Experiment	(6)	(7)	(8)	(9)	(10)	(11)
Concentration (per cent).....	10	5	2	1	$\frac{1}{2}$	$\frac{1}{4}$
Approximate number of days to form gels.	40	14	90	125	200	—

(9) was still rather a weak gel after 125 days; (10) eventually set, but (11) remained mobile after 12 months' exposure. Initial exposure was in March, and the tubes were sealed with about 10 per cent of their volume occupied by air.

In another series the air was removed by boiling off part of the solvent under reduced pressure. The concentrations of the rubber sols were 10, 7.5, 5, 3.5, 2 and 1 per cent. All were dissolved in carbon tetrachloride-acetone mixture containing 0.2 per cent of benzophenone to accelerate gelling. The two more concentrated solutions, i.e., 10 and 7.5 per cent, were the last to show signs of gelling, the first effect of the light being to reduce the viscosity. On the second day all were gelled, the more concentrated solutions completely, the more dilute partially; the gel forming in the body of the liquid and on the side of the tube exposed to the light.



It is noteworthy that, in both series of experiments, concentrations in excess of 5 per cent took longer to gel; the first effect of exposure was to reduce all the sols to the same low viscosity. This, of course, takes longer with more concentrated sols, as they are originally more viscous and less completely dispersed. In the substantial absence of oxygen, there is little difference in the time taken to gel the remainder of the sols, that is (8) to (10) but, in the presence of air, the weaker the solution the longer the time taken. This may be ascribed to the larger proportion of oxygen relative to rubber in the weaker solutions, as the air space was as nearly as possible the same in all the tubes in Table II. Photogels can be prepared from solutions much weaker than one-half per cent under suitable conditions with a sufficiently active sensitizer.

As ketones are sensitizing agents, a parallel series of experiments were made using throughout, as solvent, 2 parts of carbon tetrachloride and one part of each ketone. The results are set out in Table III.

TABLE III

	(1)	(2)	(3)	(4)	(5)	(6)
Ketone	Dimethyl	Methyl ethyl	Diethyl	Methyl phenyl	Diphenyl	Control no ketone
Time taken to form gel (days) . .	14	14	26	12	5	30

The exposures were made in March. There is perhaps more difference between (3) and (6) than would appear from the figures, as (6) is a weaker gel. Thickening on the surface was noted on the third day in the case of (4), and formation of a blob of gel on the wall of the container on the side exposed to light. Pummerer states that gel formation starts on the surface, but this has not been observed; rather only some thickening or increased viscosity. Where only part of the liquid has gelled, it is usually below the surface and on the side exposed to the light.

There is no simple relationship noticeable between the various ketones, but benzophenone is by far the most active. It is, however, exceeded in activity by some higher ketones or quinones, anthraquinone and anthrone being perhaps the most active of any so far examined. As is well known, these substances exhibit more of a ketonic than quinonic character. In conformity with this, benzoquinone was found to be ineffective. It actually prevents gelling. On the other hand, the substituted quinones such as 1,4-naphthoquinone and chloranil are powerful sensitizers. A list is given of some of those which have been tried, both in carbon tetrachloride-acetone mixture and in ligroin solutions. The order of efficiency is as follows: chloranil, anthraquinone, xanthrone, benzophenone, 1,4-naphthoquinone and benzaldehyde. All of these, except chloranil, dissolve eventually in a rubber solution in ligroin. It is probable that chloranil would prove the most active with a liquid in which it is sufficiently soluble. The carbon tetrachloride-acetone solvent mixture is itself a sensitizer, and levels the action of other sensitizers. In these experiments 15 per cent of sensitizer (calculated on the rubber) was used with the carbon tetrachloride mixture, and 5 per cent with the ligroin.

In another series of experiments, with ligroin solutions in evacuated tubes, the quantity of sensitizer was varied over a wide range to ascertain the amount necessary to bring about the formation of a photogel. The time taken was less, the greater the proportion of sensitizer. One per cent of benzophenone and 5 per cent of benzaldehyde (calculated on the rubber) were just sufficient to cause



gelling. Rather less caused increased viscosity but, with 1 per cent or less, no appreciable change took place with any sensitizer, and the contents of the tubes were quite mobile after several months' exposure in summer. Small quantities of sensitizers are therefore quite ineffective in an inert solvent, such as ligroin.

In some cases a color change is noted after long exposure. If a trace of air is present or carbon tetrachloride-acetone mixture is used, darkening always takes place, and the resulting photogel is yellow or reddish brown. The syneresis liquor remains colorless. When using ligroin in a vacuum, the gels are almost invariably colorless. The only exceptions are anthraquinone, pale greenish yellow and chloranil, dark brown. In two cases a photogel appeared to liquefy on prolonged exposure. This could not be attributed to access of air in either case, since no crack could be detected in either of the sealed tubes.

*Summary.*—Formation of a photogel is preceded by loss in viscosity when air is present. The air also delays gelling. The more air the longer the time taken to gel. Gelling is slow in some solvents, particularly benzene and ligroin. No gelling takes place in the latter *in vacuo* in a sealed tube without additional sensitizer. Gelling is relatively rapid in some halogenated solvents, particularly carbon tetrachloride. In the presence of sensitizers, such as ketones and quinones, the time of gelling is greatly reduced, and may be 4 hours or less in sunlight. Benzoquinone is an exception. The amount of sensitizer required to produce a definite effect in ligroin is appreciable, being not less than 1 per cent on the rubber and usually 5 per cent or more.

*Comparative gelling properties of different types of rubber.*—The type and condition of the rubber has little influence on the rate of gelling. In Table V among other data are given the times taken by crepe rubber, variously treated, to gel in four different solvents or solvent mixture, that is, (1) unmilled, (2) milled to moderate extent, about 20 minutes, as for rubber manufacture, and (3) cold milled for 1 hour. It will be seen that there is no appreciable difference in the rate of gelling of the three samples in any of the solvents, except in the case of the unmilled rubber, which generally took a little longer than the milled. The tubes were sealed with air spaces above, and the additional time taken for the unmilled crepe rubber to gel appeared to be that required completely to disperse the rubber and to reduce the viscosity of the solutions before the tendency to gel became effective. It appears, therefore, that a reduction in the length of the thread-like rubber molecule, which is generally believed to result from milling, does not influence the formation of the presumably three-dimensional aggregates which are usually supposed to account for the formation of gels. As the well-milled rubber was easiest to disperse, it was preferred, and the same milled sample was used throughout the work here recorded, except for experiments with sol fractions and specially purified rubber, which will now be described.

The rate of gelling of these rubbers was determined both in the presence of air and sealed *in vacuo*, using a mixture of carbon tetrachloride and acetone as solvent and sensitizer.

A series of sol fractions numbered 2 to 6 were obtained by extraction of raw smoked sheet rubber with ligroin, and a similar series with benzene in a continuous extraction apparatus in a current of carbon dioxide. These fractions may differ fundamentally from similar fractions obtained from purified rubber, but, at least, they represent a series of specimens of diffusion rubbers almost free from nitrogen. They were about two years old, and had been stored in the dark without any special precautions. Neither the ligroin nor benzene-sol fractions, which appeared to be in good condition, showed any tendency to insol-

bility, although Staudinger<sup>7</sup> states that such sols under these conditions become insoluble. The rates of gelling of the ligroin fractions were found to be irregular. The middle fractions gelled simultaneously, both in the presence of a little air and in the absence of air, whereas fractions 2 and 6 took longer, particularly fraction 6.

In the similar series, consisting of benzene sol fractions, the results were more regular. The fractions gelled in ascending order, although the differences were not great. Five fractions were used, *i.e.*, fractions 2 to 6. These specimens show the reverse order of gelling to that obtained by Pummerer, who, with four fractions obtained by fractionation with ethyl ether from alkali purified rubber, found that the higher the fraction the quicker it gelled. None of the fractions from smoked sheet gelled faster than well milled crepe rubber. As the higher fractions give more viscous sols and, as the first effect of irradiation is to reduce the viscosity, the order of gelling of this series of fractions is in accordance with anticipation.

Experiments were also made with specially prepared rubbers, including (1) a sample from centrifuged latex which had been dialyzed until entirely free from diffusible substances, (2) a sample<sup>8</sup> of crepe rubber from triple creamed latex, third fraction coagulated with acetic acid, and (3) a commercial low nitrogen rubber prepared from latex. All these highly purified rubbers behave normally when irradiated but, in general, took a little longer to gel than ordinary crepe rubber.

In another series comparative tests were made with two specimens of rubber prepared from alkali treated latex which were dialyzed till free from alkali, and one of these subsequently acetone-extracted. As controls were used sample (2) above, the same after acetone extraction, and the well milled crepe rubber taken throughout as standard. Six tubes were evacuated by boiling off a little of the solvent under reduced pressure and sealed. They were kept in the dark, except when taken out once or twice a day and vigorously shaken. Some specimens dissolved more readily than others. Dispersion was complete in about 10 days. They were then exposed in sunshine in the window and after 6 hours the contents of every tube was a firm gel. Under comparable conditions, therefore, well-milled crepe rubber forms a photogel as fast as, or faster than, any other used in these experiments.

*Summary.*—Milling, even excessive milling, of rubber does not reduce the time taken to form a photogel. In all cases in the presence of air a reduction in viscosity precedes gel formation. Some purified rubbers may take a little longer to gel. Some sol fractions also gel more slowly. The time taken to form a gel was irregular, and most of the fractions gelled on the same date. The time taken probably depended on the viscosity or completeness with which the rubber was dispersed. The lower the viscosity the quicker is the rate of gelling.

The length of the molecule, as ascertained by the viscosity of the sol, which in its turn is determined by the intensity of the milling or the number of the sol fraction, has therefore no influence on the rate of gelling. When viscosity is reduced to a common level, the rate of gelling varies little. Purification of the rubber in the process of preparation as by alkali treatment of latex, dialysis, creaming or fractional coagulation of the latex, has no uniform effect. In any case the differences noted are small, and no specimen, however prepared, gels faster than milled crepe rubber.

*The function of oxygen in the gelling process.*—There are indications that oxygen acts as a sensitizer, for instance, a ligroin solution gels, although after a

very long interval, when a trace of oxygen is present. If oxygen is essential to the formation of photogels, a reducing agent such as hydroquinone might be expected to retard, or completely prevent, gelling. In a series of experiments it was found that hydroquinone had an inhibiting effect, but that substantial proportions were required to prevent ultimate gelling. Experiments were made with well-milled crepe rubber, and the three samples of rubber from purified latex already referred to above. The solvent was carbon tetrachloride, in which photogels gradually form without a sensitizer. The tubes were evacuated. Under these conditions 0.5 per cent on the rubber was found to be, approximately, the critical amount below which hydroquinone did not reduce the time of gelling, compared with the controls. Eventually every specimen gelled, even that with 50 per cent of hydroquinone on the rubber. Table IV gives the details, and indicates the delayed gelling of three purified crepe rubbers. The commercial low-nitrogen rubber (Goodyear) is manufactured in Sumatra by centrifuging or creaming processes. It shows the greatest resistance to gelling. The purified rubbers are also the most sensitive to hydroquinone. In the presence of sensitizers,

TABLE IV

Per cent hydroquinone on rubber	Days required to form gel with			
	Milled crepe	Centrifuged cream dialyzed	Triple- creamed 3rd fraction acid- coagulated	Goodyear low-nitrogen rubber
50	120	—	—	—
5	35	—	—	—
0.5	2	7	14	60
Nil	2	7	1	15

such as acetone, hydroquinone, delays gelling slightly. Duplicates of some of the above tubes were sealed with air. In the presence of hydroquinone, the air reduced the time required to form a gel and, in the absence of hydroquinone, it tended to increase it.

Cobalt, copper and some other metallic salts are known to act as catalysts and to promote oxidation of rubber in the presence of air. With free access of air, the action is superficially similar to that of the sensitizers already mentioned. Cobalt linoleate and copper oleate were tried in various solvents, including both ligroin and the carbon tetrachloride-acetone mixture. The general effect was to delay gelling rather than to promote it. This applies particularly to the copper salt. Eventually the contents of all the air free tubes gelled, but not all those sealed with air. Nitrobenzene and homologs are oxidizing agents, and are known to have a vulcanizing effect on rubber. Trinitrotoluene was tried in the carbon tetrachloride-acetone mixture. It prevented gelling. On the other hand, sulfur, which is known to have a protective effect on raw rubber exposed to light<sup>9</sup> caused little, if any, delay in gelling. This is contrary to the original observation of Porritt, who found that whereas the contents of his control tube gelled, that containing sulfur did not.

When a tube containing a gel formed in the presence of air is opened, peroxides can be detected. Consequently it seems probable that peroxides would act as sensitizers. Ethyl ether, to which a small quantity of barium peroxide has been added, acts as a powerful sensitizer. Benzoyl peroxide in all solvents acts similarly. This substance is a vulcanizing agent. It also rapidly increases the plasticity of a rubber mix, and in the presence of air reduces the viscosity. In

irradiated solutions it was found to be somewhat less efficient than benzophenone and other very active sensitizers but, unlike these, it causes the formation of a gel in the dark, both in an evacuated tube and when sealed enclosing a small quantity of air. The quantity of peroxide required to produce a gel under these conditions is considerable. Using the tetrachloride-acetone mixture as a solvent, 100 per cent of peroxide on the rubber is necessary to form a gel within a few days in the dark, and a couple of months is necessary with 20 per cent. Five per cent is insufficient, although the viscosity of the solution is reduced. Still smaller quantities appear to have no effect whatever. Twenty per cent of the peroxide in ethyl ether solution formed a gel in the dark in about three months, but a similar ligroin solution was entirely unaffected after several months. No gel formation in the dark has been observed with other sensitizers, in spite of experiments over prolonged periods. Photogels formed with smaller proportions of benzoyl peroxide by irradiation show properties identical with those produced by other sensitizers, and gels formed by means of benzoyl peroxide in the dark do not appear to differ from photogels prepared with any other sensitizer.

Parallel experiments in the dark and with exposure to light led to the conclusion that the effect of benzoyl peroxide is roughly proportional to the amount used, but less than 1 per cent on the rubber has no effect on the formation of a photogel. Similar results are obtained with benzophenone and other sensitizers. But whatever the sensitizer, solutions in ligroin are the slowest to form photogels, and these sols do not gel unless the proportion of sensitizer is substantial. On the other hand, solutions containing acetone mixed either with ethyl ether or carbon tetrachloride form gels in a few days, but again the rate of gelling is not accelerated by sensitizers unless present in substantial proportion. It appears, therefore, that gel formation is accelerated by some product which is formed on irradiation between the sensitizer or acetone and the ethyl ether or carbon tetrachloride, but that benzene and ligroin, being relatively inert, do not readily form photogels. These conclusions are confirmed by a study of the yields of dry gel referred to later.

*Summary.*—Although oxygen may act as a sensitizer, hydroquinone, except in substantial amounts, does not delay the formation of photogels, and even 50 per cent on the rubber does not prevent it. Purified rubbers are more susceptible and 0.5 per cent of hydroquinone on the rubber causes a few days' delay. Sulfur, which is known to act as an antioxidant, has no effect. Oxidising catalysts for rubber, such as cobalt linoleate and copper oleate, do not promote gelling but delay it, particularly in the presence of a little air. Benzoyl peroxide in high proportion causes gelling in the dark. In light, its efficiency is hardly as great as benzophenone.

*Nature of the photogels.*—The gels vary in consistency. Those obtained with difficulty and only after a long period of irradiation such as with benzene or ligroin, without acetone or other sensitizer, are tenuous and adhesive. They are rapidly reconverted to liquids on exposure to light and air. Gels formed rapidly, particularly after further exposure, are tough and elastic, easy to handle, and can be cut cleanly with a knife or scissors. The rubbers recovered from the gel by evaporation of the solvent in an inert atmosphere vary in properties, but generally photogels, when freed from solvent, are soft, distensible, and recover fairly well, although slowly, after stretching. Some data regarding swelling properties are given later but, broadly speaking, although the dried gels resemble vulcanized rubber in that they do not freeze in ice water and are more resistant to prolonged heating, say, at 100° C than raw rubber, their physical properties

are much inferior to vulcanized rubber. Some will stretch 700 to 800 per cent before rupture, but final recovery is slow, and there is no "snap". The tension, when stretched, is low. In some respects they resemble soft vulcanized rubber which has imbibed some solvent.

Pummerer has assumed that photogels consist merely of rubber in which some of the molecules have become united by the formation of carbon bridges, although the iodine number showed little change. It is now suggested that photogels consist of more complex derivatives.

That the formation of a photogel is not a mere change in the physical properties of the raw rubber is apparent from the yield of gel from a given quantity of rubber. There is almost invariably a substantial increase in weight, as will be seen from Table V. This table includes the figures showing the time taken to form gels. The small losses shown for samples (1a), (1b) and (1c) probably result from loss in transference of the gels, which in all these specimens were weak, soft and sticky. They were white. The corresponding gels (2a), (2b) and (2c) were stronger and more elastic and faintly yellowish. The remainder were still tougher and also darker, particularly (4). The gels were dried at approximately 100° C until they no longer lost weight.

TABLE V

Solvent	(a) Unmilled crepe				(b) Milled crepe				(c) Heavily milled crepe			
	(1)	(2)	(3)	(4)	(1)	(2)	(3)	(4)	(1)	(2)	(3)	(4)
Days taken to form gel .....	51	39	31	6	43	33	21	6	42	33	21	6
Weight of dry gel.												
Original rubber												
= 100 .....	98.1	102.2	111.5	121.5	98.9	103.7	112.9	129.6	98.7	111.7	118.3	126.1

Solvent.—(1) Benzene; (2) benzene 2 vols. + acetone 1 vol.; (3) carbon tetrachloride; (4) carbon tetrachloride 2 vols. + acetone 1 vol.

It is seen that, generally, the shorter the exposure required to form a gel, the greater the increase in weight; also the greatest increase occurs with the chlorinated solvent. In the presence of acetone, which acts as a sensitizer, the increase varies from 20 to 30 per cent. Such increases cannot be accounted for by oxidation as the amount of air sealed in the tube would be wholly insufficient. The increase in weight would imply the absorption of about one atom of oxygen for every  $C_5H_8$ -unit, and with much less than this rubber is converted into a resin, with complete loss of all its elastic properties. In solvent (3) the increase is approximately 10 per cent and, as the solvent was carbon tetrachloride alone, it seemed probable that these photogels must contain a substantial amount of chlorine. This was found to be the case.

*Summary.*—Photogels vary in consistency according to the amount of irradiation and the nature of solvents and sensitizers. Similarly the rubbers recovered from the gels by evaporation of the solvent vary in properties, *viz.*, are tougher and harder the stronger the gelling properties. The recovered rubbers show an increase in weight which cannot be attributed to oxidation. When carbon tetrachloride is used as a solvent the recovered rubber contains chlorine. The recovered rubber resembles vulcanized rubber in some respects, but is much softer and weaker.

*Halogen content of photogels.*—A tube made up in April exactly as (4c) (see Table V) required approximately one week to form a gel. It was exposed for a total of about three months and was put away and not opened till the following



year. The gel was firm and strong enough to bear removal from the tube without rupture. It was transferred to a larger tube and dried at about 100° C in a current of carbon dioxide until the weight was constant. The dry product was soft and elastic, but no tougher than raw rubber. It could be torn up with the fingers and elongated, as far as could be estimated, to about three or four times its original length before rupturing. A portion was set aside for analysis and the bulk exhaustively acetone-extracted. A portion of this was again set aside for analysis and the remainder, after cutting into small pieces, was boiled for two working days with normal alcoholic potash solution, washed exhaustively, dried, weighed and analyzed.

The literature contains little information on the estimation of chlorine in rubber, and a number of trials were made by different methods. The fusion method of Henriques gives low results. Fusion with caustic potash and sodium peroxide as recommended by Caspari<sup>10</sup> is more satisfactory, but unpleasant to carry out. The method found most satisfactory is due to Robertson, in which the specimen is distilled with a chromic acid mixture. The chromyl chloride and chlorine are absorbed in a solution of sodium peroxide. It is, however, necessary to use more chromic acid than is usually recommended for the purpose; 8 grams of potassium bichromate and 40 cc. of concentrated sulfuric acid for 0.25 gram of rubber. A blank was carried out on the milled crepe rubber used, and the figure obtained was subtracted from those given by the irradiated specimens in arriving at the results recorded. The amount of chlorine present in crepe rubber is almost negligible compared with the chlorine found in irradiated products in which a halogenated solvent was used.

If the weight of the original rubber is 100, the figures in Table VI record the increased weight and the combined chlorine.

TABLE VI

	Weight of dry gel (Original rubber) =100	Chlorine content (Per cent)
Dried gel .....	161.8	14.7
Dried gel after acetone extraction.....	156.4	12.2
Dried gel after acetone extraction and alcoholic potash extraction .....	146.2	9.2

There was little difference in the physical condition of the rubber after the various stages of extraction.

It is seen that the increased weight of the above gel is only partly accounted for by the chlorine contained in it. A small part of this is removed by acetone extraction and a further part by alcoholic potash extraction. The greater proportion remains, indicating that the chlorine is as firmly held as in rubber vulcanized with sulfur chloride, from which also a part of the chlorine can be removed by boiling with alcoholic potash.

The experiment was repeated with a larger quantity of rubber (10 grams) in a flask, evacuated and sealed. Simultaneously an experiment was made using carbon tetrachloride alone, and a third experiment similar to the first with 5 per cent of anthraquinone on the rubber as an additional sensitizer. The exposures were in June to August. The results in Table VII were obtained:

The dried gel of (3) may contain a part of the anthraquinone. The increases in weight are much smaller, as is also the chlorine in combination, than in the previous experiments, owing to the shorter period of irradiation and the greater



depth of liquid. Frequently the gel may be seen to grow from the walls of the vessel on the side exposed to light. From this it appears that formation of a gel from a bulk of fluid takes place gradually as the actinic rays penetrate the fluid. Although the increase in weight and chlorine in combination are similar for (1) and (2), the properties generally show a progressive change with time taken to gel; and the effect of the additional sensitizer in (3) is evident in all respects.

Similar results are obtained in the presence of small quantities of air. Thus, in various experiments, using the mixture of carbon tetrachloride and acetone, and after extraction of the dried gel, increases in weight of 22.4 per cent with a chlorine content of 12.8 per cent, and 21.3 per cent with a chlorine content of 14.5 per cent, were observed. With acetophenone instead of acetone, an increase of 16.8 per cent in weight and a chlorine content of 11.8 per cent were noted, and with benzophenone an increase of 12.6 per cent and a chlorine content of 8.1 per cent. Many other similar figures have been obtained. In a comparative

TABLE VII

Solvent and sensitizer	(1) Carbon tetrachloride	(2) Carbon tetrachloride and acetone	(3) Carbon tetrachloride acetone and anthraquinone
Days taken to form gel.....	17	1	0.5
Total days' exposure.....	104	44	43
Nature of gel.....	Soft and sticky	Firm, not sticky	Stiff, not sticky
Nature of gel after drying.....	Soft and elastic	Firm and elastic	Harsh and less elastic
Weight of dried gel.....	103.9	104.5	115.3
Weight of dried gel after acetone extraction.	100.0	101.4	94.9
Chlorine in dried gel (per cent).....	4.5	4.5	—
Chlorine in dried gel after acetone extraction (per cent) .....	4.0	4.3	8.5
Chlorine in dried gel after alcoholic potash extraction (per cent).....	3.3	4.2	5.5

experiment, one tube being evacuated and another sealed with a little air, similar increases in weight were noted for both gels. The consistency and chlorine content varies with the period and degree of irradiation. When the exposure is prolonged and in the presence of powerful sensitizers, the dried gels are tough and horny, with little elasticity. The increase in weight and the chlorine contents are then high, as seen in the following figures. In these experiments the tubes were small, and held only 0.4 gram of rubber. The light had only a thin layer of solution to penetrate. In addition to the carbon tetrachloride mixture, the tube contained 0.1 gram (25 per cent, on the rubber) of the sensitizer. The results are given in Table VIII.

Doubling of the concentration of the rubber solution in the second control did not have an appreciable effect on the yield. The six gels for which figures are given were all hard, tough, dark brown specimens, with little or no distensibility. They were united, acetone-extracted, and the chlorine determined in the extracted rubber. The following figures are calculated on the original rubber taken=100:

Weight of dried gels.....	154.9
Chlorine, 27.0 per cent, equivalent to.....	41.8
Weight of acetone-extracted gels.....	132.4
Chlorine 17.6 per cent, equivalent to.....	24.2

Most of the increase in weight is seen to be due to chlorine, only 13.1 and 8.2 parts, respectively, arise from the addition of carbon, hydrogen or oxygen.

In the same series there were parallel controls sealed with a little air. Both these gelled in approximately one day, so the presence of the air had little or no effect on rate of gelling.

Most of the figures recorded above deal with carbon tetrachloride as solvent or sensitizer. Many other halogenated solvents behave similarly, although those tried were invariably less effective. The time taken to form photogels was much reduced in parallel experiments, in which one-third of the particular solvent was replaced by acetone. The results, both without and with acetone, are shown in Table IX.

TABLE VIII

Additional sensitizer or inhibitor	Days to gel	Weight of dry gel (Original rubber =100)	Chlorine (Per cent calcd. on original rubber)
Benzoquinone .....	No gelling	—	—
Anthraquinone .....	0.5	154	31.2
Benzophenone .....	1	149	33.6
Hydroquinone .....	2	132	28.3
Cobalt linoleate .....	5	—	—
Benzaldehyde .....	1	150	32.0
Copper oleate .....	75	—	—
Control, no additional sensitizer.....	1	161	52.2
Control, double concentration.....	1	162	49.2

TABLE IX

Solvent	No sensitizer			One-third vol. acetone as sensitizer		
	Days to form gel	Weight of dry gel (Original rubber) =100	Halogen (Per cent)	Days to form gel	Weight of extracted gel (Original rubber) =100	Halogen (Per cent)
CCl <sub>4</sub> .....	1	109	6.1	$\frac{1}{2}$	121	17.2
CHCl <sub>3</sub> .....	4	105	0.9	2	98*	1.2
C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> .....	44	102	2.0	7	101	0.6
C <sub>2</sub> HCl <sub>3</sub> .....	No gelling	—	—	23	104	2.9
C <sub>6</sub> H <sub>5</sub> Cl .....	30	95*	1.9	4	102	1.7
C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> .....	20	92*	1.6	4	91*	0.7
C <sub>2</sub> H <sub>5</sub> Br .....	No gelling	—	—	2	100*	2.3
C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub> .....	2	98*	3.2	1	99*	4.5
C <sub>2</sub> H <sub>5</sub> I .....	No gelling	—	—	7	104	—

It will be seen that photogels were formed with all halogenated hydrocarbons in the presence of acetone, but some of them were inactive by themselves. In some cases, marked with an asterisk, the figures apply to acetone-extracted gels, as it was found necessary to soak in acetone to remove the gels from the tubes. Where the gel has shrunk in the tube and is surrounded by syneresis liquor, the latter vaporizes readily, leaving a cylinder of gel detached from the interior walls of the tube. This cylinder gradually shrinks and is, in consequence, easily removed for weighing and analysis. In other cases, particularly with weak gels, they remain adhering to the walls of the tube, bubbles form in the mass, and the contents tend to bubble out of the tube. In such cases it is necessary to place the opened tubes in an excess of acetone; the solvent diffuses out into the acetone and the gel shrinks. As a result the drying can be completed without loss. There

was pronounced syneresis in most of the tubes. In some the gel had contracted to half its volume. The mobile syneresis liquors contained only traces of rubber or none at all. They were always colorless, even in the case of tubes prepared with ethylene dibromide, indicating the absence of free halogen. By treating the acetone extracted gel formed in carbon tetrachloride with more carbon tetrachloride in the cold, a fractionation was effected after four months. The carbon tetrachloride-soluble part had a chlorine content of 13.6 per cent; the insoluble 13.9 per cent. It was concluded that no separation of the components had taken place and that the chlorinated rubber had dissolved as a whole, indicating homogeneity of the product.

*Summary.*—The chlorine content of a photogel formed in carbon tetrachloride solution may amount to 50 per cent of the weight of the original rubber, but the combined chlorine does not account for the whole increase in weight. Many other halogenated solvents give halogenated products, but the increase in weight shown and the halogen content are smaller than with carbon tetrachloride. Acetone extraction removes only a small part of the dried gel, and the residue contains most of the chlorine. Alcoholic potash removes rather more chlorine, but the greater part is retained by the rubber, indicating that it is as firmly held as in a rubber vulcanized with sulfur chloride.

TABLE X

Benzoyl peroxide per 100 pts. rubber	Gelled in dark 20	Gelled by exposure to light					
		80	20	4*	0.8	0.08	0.008
Weight of dried gel							
After acetone extraction....	108	160	111	111	104	113	116
After alc. KOH extraction...	96.7	94	98	94	99	103	99
Chlorine in dry gel (per cent).	8.7	28.0	11.2	8.5	10.7	9.5	7.8
After acetone extraction....	6.0	29.1	12.5	7.5	9.8	9.1	6.8
After alc. KOH extraction...	5.3	22.4	10.9	8.5	8.9	9.6	7.2

\* Tube cracked.

*Benzoyl peroxide as a sensitizer.*—It has already been shown that benzoyl peroxide causes gelling of a rubber solution in the absence of light, if present in proportions of 20 per cent and upwards, calculated on the rubber. In all respects the product resembles that obtained by irradiation. Table X shows the weight relationship of the rubber taken after extraction of the gel with acetone and alcoholic potash and the chlorine content of the dried and extracted gels. The table also contains comparable figures for a number of photogels obtained with varying proportions of benzoyl peroxide. The rubber was dissolved in the usual mixture of carbon tetrachloride and acetone. Gelling took place in the presence of a little air above the surface of the liquid in the tubes. In the dark the gel took a couple of months to form, and the tube was not opened till about a year after it had been sealed. The tubes in the light were exposed for several months; all for the same period. The conversion, as shown by increase in weight and chlorine content, is less in the gel formed in the dark than in that produced by irradiation with the same proportion of benzoyl peroxide. The increases in weight are irregular, except that much higher figures are obtained when 80 per cent of benzoyl peroxide was used. The chlorine figures show more regularity. Those with 4 per cent of benzoyl peroxide are lower than the others and out of order. This may arise from slight damage to this particular tube, resulting in a small air leak, and causing some softening or liquification of the gel on the surface. The conclusion is drawn that the action of benzoyl peroxide in the dark is similar

in nature, but somewhat less in degree, to that in the light, both in composition and physical properties. The products, as with other dried photogels, are quite unlike rubber vulcanized with this agent. Benzoyl peroxide is also an efficient sensitizer if used in the preparation of photogels with other solvents, particularly ethyl ether. Twenty per cent on the rubber gave a gel on one day's exposure in this solvent. After irradiation for a few months, this gel gave an increase in weight of over 50 per cent on the original rubber and a 12 per cent increase after acetone extraction. Smaller increases, or none at all, were obtained with

TABLE XI

Solvent	Sensitizer (per cent calcd. on rubber)	Proportion of rubber soluble in 10 days	Swelling index
(1) Carbon tetrachloride and acetone	Benzoyl peroxide 20 per cent (sample in the dark, see Table X)	0.26	11
(2) Carbon tetrachloride and acetone	Benzoyl peroxide 20 per cent (sample in the light, see Table X)	0.07	8
(3) Carbon tetrachloride and acetone	Benzophenone 5 per cent (tube evacuated)	0.19	12
(4) Carbon tetrachloride and acetone	Benzophenone 5 per cent (tube containing air)	0.14	10
(5) Carbon tetrachloride and acetone	Anthraquinone 5 per cent (see (3), Table VII)	0.13	14
(6) Carbon tetrachloride and acetone	Anthraquinone 5 per cent (after milling)	0.47	12
(7) Carbon tetrachloride and acetone	Nil (see (2) Table VII).....	0.35	10
(8) Carbon tetrachloride and acetone	Nil (dry gel Cl 9.8 per cent).....	0.10	10
(9) Carbon tetrachloride and acetone	Nil (ditto after acetone extraction. Cl 10.7 per cent)	0.10	10
(10) Carbon tetrachloride and acetone	Nil (ditto after alc. KOH extraction Cl 10.4 per cent)	0.12	7
(11) Carbon tetrachloride .....	Nil (see (1) Table VII).....	0.39	17
(12) Carbon tetrachloride .....	Nil (see Table IX).....	0.25	9
(13) Benzene and acetone.....	Benzoyl peroxide 20 per cent....	0.15	8
(14) Benzene .....	Benzoyl peroxide 20 per cent....	0.18	19
(15) Ethyl ether and acetone...	Benzoyl peroxide 20 per cent....	0.04	16
(16) Ligroin and acetone.....	Benzoyl peroxide 20 per cent....	0.22	14
(17) Chloroform and acetone...	Nil .....	0.20	23
(18) Ligroin .....	Anthraquinone 5 per cent.....	0.05	12
(19) Ligroin .....	Benzophenone 5 per cent.....	0.28	19
(20) Ligroin .....	Benzaldehyde 20 per cent.....	0.43	18
(21) Ligroin .....	Nil .....	0.50	33

benzene, a mixture of benzene and acetone, and the corresponding mixture of ligroin and acetone. In the absence of acetone, a gel was not always obtained with ligroin *in vacuo*. These results indicate that with a variety of solvents benzoyl peroxide acts like other sensitizers in the production of photogels.

*Solubility and swelling properties of photogels.*—Whereas properly vulcanized soft rubber is almost completely insoluble in cold benzene in the dark, photogels are not completely insoluble. They swell considerably, like vulcanized rubber. These properties have been used as a criterion of degree of vulcanization or "enhanced polymerization" by Spence and Ferry<sup>11</sup>. In their experiments, rubber in purified latex form was treated by heating with potassium ferrieyanide or by irradiating in closed tubes in the presence of sensitizers, including benzoquinone,

1,4-naphthoquinone and benzaldehyde. Having regard to the similarity in technique adopted by Spence and Ferry and that used in the preparation of photogels, it was of interest to compare the solvent and swelling properties of the latter with the products obtained by Spence and Ferry. A number of photogels after evaporation of the solvent were swollen in 100 times their weight of benzene in the dark. After three days the benzene with any dissolved rubber was decanted and replaced by further benzene, the whole being set aside in the dark for a further week, when the supernatant benzene was decanted and united with that first removed. The whole was then evaporated to dryness and weighed. The swollen gel was also weighed and the results expressed as proportion soluble in ten days and as swelling index. This latter is the volume of the gel (cc.) divided by the weight of the rubber in grams. Spence and Ferry do not state how the volume of the swollen gel was measured. It was found convenient to weigh the swollen gel and calculate the volume from the specific gravity of the solvent.

In this way the figures in Table XI were obtained for a number of photogels.

The figures for the gels formed in ligroin (18) to (21) give higher figures for the swelling index and proportion soluble than most of the others. The last sample (21) formed without sensitizer gave by far the highest figures. It has been stated that gels do not always form in this medium. Of three tubes put on simultaneously, two eventually gelled, and (21) is one of them. A high figure is also given by benzene. From these results it is clear that those gels formed in hydrocarbon solvents without sensitizers are the least altered, their swelling capacity tending to be unlimited, like the rubber from which they are derived. The physical weakness of these gels is in conformity with these properties; as also the ease with which they are oxidized on exposure to air and reconverted to sols, and the negligible increase in weight shown by the dry gel over that of the rubber taken.

The figures for swelling index and solubility of the photogels in Table XI are of a similar order to those shown by the products obtained by Spence and Ferry by irradiation of purified latex in the presence of sensitizers. There is no obvious relationship between the figures for proportion soluble and swelling index. The effect of milling has been to increase somewhat the proportion soluble (sample (5)), but has had no appreciable effect on the swelling index. Other specimens of dried photogels which have been milled show no great change. In this connection Pummerer and Kehlen<sup>4</sup> reported that milling reconverted a photogel to the original soluble condition of the sol rubber.

*Discussion.*—A theory to account for the formation of photogels, particularly the increase in weight over that of the rubber taken, and the retention of halogens when a halogenated solvent is used, must take the following experimental data into consideration. (1) The increase in weight is specific to the solvent and is greater the longer the period of irradiation. (2) The increase is much the same in the presence of a small amount of air as in the absence of air. (3) The presence of more than a trace of air delays gelling; the greater the proportion of air the greater the delay, but once gelled the properties of the gels are similar. Peroxides can be detected when the tubes are opened. (4) There are relatively small differences in the rates of gelling of differently prepared rubber, although a higher degree of purification of the hydrocarbon does in some cases delay gelling. (5) Mastication or milling of the original rubber has little influence on the rate of gelling, or on the consistency of the gel, or the increase in weight. It tends to reduce the time taken to form a gel when air is present. (6) In the case of a viscous sol, and in the presence of light, and of a little air, a reduction in vis-



cosity takes place before gelling begins. In the absence of air, no reduction in viscosity is usually apparent, and gelling may begin from the time the tube is sealed and before the rubber is completely dispersed. (7) The halogen content may account for almost the whole of the increase in weight or more generally a lesser part. (8) Some halogen solvents, particularly carbon tetrachloride, cause rapid gelling and substantial increase in weight, whereas others such as chloroform cause only slow gelling, a weak gel, little or no increase in weight and little halogen retained in the gel. (9) The halogen is strongly bound, the halogen content is often hardly affected by acetone extraction, and only a small portion is removed by alcoholic potassium hydroxide extraction. (10) The dried chlorinated products do not give the carbylamine reaction. According to Kraft and Merz<sup>12</sup>, the carbylamine reaction is given by carbon tetrachloride as well as by chloroform. Such a reaction is difficult to formulate, and in the authors' opinion the odor obtained with carbon tetrachloride is not typical of carbylamine, but is less unpleasant and much fainter. However, none of the dried rubber gels prepared with either carbon tetrachloride or chloroform gave the slightest odor when heated with aniline, alcohol and potassium hydroxide. (11) The products swell, but are only partly soluble in cold benzene in the dark. Milling the gel increases the proportion soluble, but has little effect on the swelling properties. (12) The products resemble vulcanized rubber in that they do not freeze in ice water and can be heated in air for a prolonged period at, say, 100° C without much change, and do not become sticky by this treatment as raw rubber would. (13) The products of moderate reaction are physically more like raw rubber than vulcanized rubber, being soft, weak and distensible. They are easy to stretch, have low modulus, and are readily torn between the fingers. They have no snap. (14) When heated strongly, the products decompose and distil, much as raw rubber does, but with more difficulty, and leave more carbonaceous residue.

There are three alternative suggestions which can be put forward in explanation of the composition of photogels: (1) They may consist of rubber which has been converted from sol to gel form through enhanced polymerization, cyclization, or formation of bridges to yield three-dimensional molecules, the function of solvent and sensitizer being of the nature of true catalysts, and the increase in weight being accounted for by physical retention of a part of the solvent, with or without sensitizer. (2) A similar explanation to the foregoing, but assuming that the solvent, with or without sensitizer, has undergone some chemical change as the result of irradiation, which change has no direct connection with the gel formation. The increased weight and chlorine content of the gel will be accounted for by the retention of substances formed by the irradiation of solvent and/or sensitizer *per se*. This alternative requires that the substance formed is non-volatile or at least difficultly volatile and acetone-insoluble. (3) Photogels may consist of products formed by reaction between the rubber hydrocarbon and the solvent and/or sensitizer. A reaction might also take place between the non-hydrocarbon components of the rubber and the solvent and/or sensitizer.

The first suggestion appears extremely unlikely. In some cases the gels were cut up into small pieces and heated for three days in a water oven in a current of carbon dioxide. It is hardly possible that anything but a trace of volatile solvent would be retained under these conditions. Further, of the points enumerated above (1) and (10) to (13) are all evidence against this suggestion, and it may be dismissed.

The second explanation is more plausible. It is quite likely that irradiation may lead to the photosynthesis of some non-volatile or difficultly volatile sub-



stance from the solvents, particularly in the presence of a sensitizer. This would not conflict with points (1) to (8). The product formed by reaction of solvent with itself or with the sensitizer, if present, would have to be unaffected by acetone extraction, as this seldom accounts for a much larger proportion of acetone-soluble substances than is found in the original rubber. It would also require to be, for the greater part, resistant to long boiling with alcoholic potash (9). The formation of a photogel would then be a matter quite apart from the increase in weight and the presence of firmly bound halogen. The suggestion is not in accord with points (11) and (12), as the formation of a byproduct would provide no explanation of the concomitant change in the physical properties of the dried photogels and the degree of irradiation; and, of course, it would not help in the least to elucidate the phenomenon of gelation in light.

To obtain further evidence on this matter, four tubes were filled with solvents and sensitizers without any rubber. The tubes were evacuated, sealed and exposed to light for three months in exactly the same way as the rubber solutions. The solvents and sensitizers used were as follows: (1) carbon tetrachloride alone; (2) the same mixed with acetone; (3) the same as (2) but containing half a gram of benzophenone, and (4) similar to (3) but benzophenone replaced by benzoyl peroxide.

The conditions and appearance of the tubes when opened were unaltered except that (3) and (4) were a little yellowed. The solvents were distilled off under reduced pressure with the following results: (1) the whole of the liquid distilled off at a low temperature, leaving no trace of residue; (2) behaved similarly, but a trace of residue remained, not volatile at 100° C, in which chlorine could be detected; (3) the contents were similarly volatile, leaving a residue of 0.442 gram of solid material, mainly unchanged benzophenone. The greater part of this was volatilized by heating in an oven well below 100° C. The remainder, 0.070, was a hard brown mass soluble in acetone, and contained 6.6 per cent of chlorine; and (4) resembled (3), leaving a solid non-volatile dark brown residue which, however, only contained a trace of chlorine.

These results indicate that, although the pure solvent remains unchanged on irradiation, a trace of photosynthetic substance is formed in the presence of acetone and other sensitizers. The nature and amounts found do not appear capable of explaining the substantial increases in weight shown by photogels or the large chlorine content of some of them. The experiments furnish no explanation of the increase in weight and chlorine content of a gel formed in carbon tetrachloride alone, as this solvent appears unaffected by irradiation. The amounts of substances formed in the other cases are inadequate to account for the increase in yield of dry gels. The greatest reaction in the absence of rubber appears to take place in the presence of benzophenone (3). This product would account for an increase in weight of a rubber gel prepared from the usual 2 grams of raw rubber of 3.5 per cent, and a chlorine content of about 1.7 per cent. As, however, the products formed from the solvents and sensitizers alone are readily soluble in acetone, these products would not account for any increase in weight, or for the chlorine content of acetone-extracted photogels. Figures are recorded (see Table VIII) of specimens without additional sensitizers, showing an increase in weight as high as 60 per cent, and a chlorine figure of 50 per cent. Six samples united and acetone-extracted gave a chlorine content of 24.2 per cent, based on the original rubber. Table VII gives the results of three similar photogels, in one of which carbon tetrachloride was used without sensitizer, this giving a figure for the acetone-extracted gel of 4.0 per cent, a similar figure of 4.3 per

cent when gelled in the presence of acetone, and 8.5 per cent in the presence of anthraquinone. In all cases the acetone extraction was very thorough, being carried on for two or three working days in the American Society for Testing Materials or British Standard type of extractor.

The conclusion is reached that, although some of the dried photogels may be contaminated with small quantities of the photosynthetic by-products formed from solvent and sensitizer without the agency of the rubber, they do not materially affect the conclusions drawn. They do not apply to figures relating to acetone-extracted gels, or to photogels formed without the addition of a sensitizer. Nevertheless, the fact that some photosynthesis takes place in the presence of sensitizers without the agency of the rubber, necessitates further investigation. There is also the possibility that the non-hydrocarbon components of the rubber may play a minor part.

Whenever a new product is obtained from raw rubber by some agency which alters the rubber by rendering it insoluble or less soluble in solvents and more indifferent to temperature changes, there is a tendency to attribute the alteration observed to vulcanization. This term has today a much broader connotation than was the case twenty or thirty years ago. The old empiricist, if handed a sheet of rubber, could soon tell by stretching it over his two thumbs or betting his teeth into it whether or not it was vulcanized; and he had no doubt that his verdict would be confirmed by freezing or solubility tests. Today the tensile properties are given less consideration, and the separation of a gel is often regarded as sufficient evidence to warrant the application of the term vulcanization. It would seem more natural to restrict this term to rubber so modified that it not only shows greater indifference to changes of temperature and attack by solvents, but also enhanced tensile properties; in particular a capacity to stretch to many times its original length and, more important still, the power to retract to approximately its original dimensions in a very short time. By such a definition, dried photogels are not a variety of vulcanized rubber. The physical properties are little if any better than those of the unmilled rubber used as the starting point, and certainly are inferior to a piece of unmilled smoked sheet. They exhibit no snap, but are soft and plastic. This change may be produced by the controlled action of many chemical reagents on raw rubber. The initial effect of these is to "spoil" the rubber from the point of view of the rubber manufacturer, without imparting to it any useful properties. Some products may result from the introduction of new elements into the rubber molecule, or from cyclization or internal linking, as shown by reduced iodine absorption. It would seem probable that the formation of a photogel is either a case of the production of a rubber derivative or cyclization, rather than a vulcanization. The changes shown as the irradiation is prolonged, and more powerful sensitizers are employed, are reminiscent of those produced by agencies such as boron trifluoride<sup>13</sup>. The first effect is a softening, accompanied by changes in solubility, followed by a gradual toughening and loss of distensibility till the product resembles raw balata. Continued reaction results in further hardening, till a hard, tough or even brittle product results. These changes have been followed in the progressive irradiation of raw rubber sols. Without sensitizers, the changes do not go beyond the soft, plastic or semiplastic stage. In ligroin and benzene solutions, without sensitizers, the dried gels are soft and sticky, and there is no ascertainable weight increase. With more active solvents, such as carbon tetrachloride, the gels are stiffer; when dried they are not more adhesive than raw rubber, and the increase in weight is substantial, *e.g.*, 5 to 10 per cent. With

sensitizers such as benzophenone, anthraquinone and others in a mixture of carbon tetrachloride and acetone, the whole range of products may be obtained, varying from the elastic, through the leathery stage to a final hard, tough mass which is not easily powdered. The change in physical properties are concomitant with increase in weight and chlorine content. An indication of the degree of conversion is also given by the degree of syneresis of the photogels. These may shrink to less than one-half their volume. Another indication is the stiffness of the recovered gel. Such gels when dry are hardly distensible, but may be so tough that a strip cannot easily be pulled in two when held between the fingers. The difficulty in obtaining the dried gel in suitable form and dimensions has so far prevented tensile testing. It is noteworthy that, although these tough inelastic products may be obtained by prolonged irradiation, no elastic intermediate stage resembling vulcanized soft rubber has been met. A third factor concomitant with the other two is the rate of gelling and the time of exposure; the greater the value of these factors the greater the increase in weight and change in physical properties.

There is a number of scattered references to the action of ultraviolet light on rubber sols which do not contain data having a bearing on the present enquiry. Reference may, however, be made to a recent paper by Srinivaran<sup>14</sup>, who irradiated purified rubber dissolved in heptane, cyclohexane, ethylene chloride and cyclohexanone, oxygen being carefully excluded. No gelling is reported, but a fall in viscosity, and a contrast is drawn between polar and non-polar solvents. The viscosity of rubber solutions in the latter was much higher than in the former, but both were reduced on irradiation; the latter approximately to that of the solvent itself, the former only slightly. It seems likely that the viscosity in the polar solvents was beginning to rise owing to the initial stages in the formation of photogels. It has already been shown that the tendency to gel formation in the non-polar solvents, ligroin and benzene is restricted, no gel being obtained in many cases with ligroin alone. The addition of acetone at once reduces viscosity and induces photogel formation in the absence of air, and photolysis accompanied by oxidation in the presence of air.

Carbon tetrachloride is an exception if regarded as a non-polar solvent. The much greater efficiency of this solvent, compared with related halogenated hydrocarbons, is also remarkable, particularly if a comparison be drawn between carbon tetrachloride and chloroform (see Table IX). The effect of the addition of acetone to benzene and carbon tetrachloride on the swelling and dispersion of smoked sheet in the dark has been studied. In both cases there was a more rapid breakdown of the structure of the rubber in the presence of acetone. In benzene, sheet rubber, which is not mechanically treated in the same way as crepe, preserves its shape, although swollen to many times its original volume. The sol hydrocarbon slowly diffuses out, but the honeycomb structure is permanent unless mechanically disintegrated. In the presence of acetone, the swelling is less pronounced, and the structure is less firm and tends to disintegrate; small pieces easily detach themselves when the upper clear layer of sol is syphoned off. The immediate object in view was to ascertain if the addition of acetone to benzene or carbon tetrachloride would enable a larger proportion of diffusion rubber to be obtained with the same amount of solvent in a lesser time. It was found that, in spite of the disintegrating effect of the acetone and the smaller volume of the swollen gel, but little advantage in separation was obtained.

Reference has been made to the work of Spence and Ferry<sup>11</sup> on the irradiation of purified latex in the presence of sensitizers, some of which are identical with those used for the production of photogels. Unfortunately they give no indica-

tion as to the yields of their irradiated products. If the changes noted by them are of the same nature as those taking place during the formation of photogels, one would expect to obtain a greater weight of rubber product than was originally taken in latex form for irradiation. Their products differ from photogels in the relatively good figures obtained in tensile tests, but it must not be forgotten that latex films, even unvulcanized, often give good tensile values. Yet the figures for swelling index of photogels and the proportion soluble in benzene indicate changes comparable with those obtained with irradiated latex. In some experiments, Spence and Ferry<sup>15</sup> have approached closely to the subject matter dealt with here. They irradiated both solid rubber in films, and rubber dissolved or swollen in benzene, in the presence of benzoquinone. They did not report any gel formation. The irradiation was carried out both in the presence and absence of air. They state that "irradiation of rubber in the swollen state with quinone produced depolymerization, even when the air was previously removed". It is probable that, had they used benzophenone or some other carbonyl compound as a sensitizer, they would have obtained, in the absence of air, the reverse effect; either polymerization or a chemical reaction leading to gel formation. Having regard to the fact that acetone is a powerful sensitizer, promoting "depolymerization" and oxidation in presence of light and air, it will be realized that it is a most unsuitable addition to a solvent for the separation of sol and gel rubber unless meticulous care is taken to prevent access of light and air. This will explain the misleading conclusions drawn by Roberts<sup>16</sup>, who used a mixture of carbon tetrachloride and acetone for the separation of the components of raw rubber. The fraction which he termed caoutchol and assumed to be a new component of rubber was, in fact, an oxidation product<sup>17</sup>.

It has been shown in this paper that benzoquinone does not act as a sensitizer, but as a retarder of gel formation. It is also worth noting that the experiments in which Spence and Ferry obtained enhanced polymerization of latex rubber with benzoquinone, the effect was much less marked than with other sensitizers such as benzaldehyde, benzophenone and 1,4-naphthoquinone. These latter sensitizers were similarly effective with rubber sols. In this connection reference may be made to a statement of Staudinger<sup>18</sup> that sol rubber irradiated in the absence of air shows increased viscosity when dissolved, and the solution may yield an insoluble gel. Unfortunately no experimental data are given, but if a rubber sol in an inert solvent such as ligroin or benzene forms a gel when irradiated in the absence of air, a similar change may well take place with solid rubber, particularly if the surface exposed is large and irradiation is carried on for a long period. The presence of a sensitizer merely accelerates the change. But having regard to the behavior of rubber, even after purification, the change in solubility may arise from a chemical reaction involving some other substance, and is not necessarily an oxidation or linking of long molecules by oxygen bridges. Consequently the conversion of solid rubber to an insoluble modification without sensitizers may be expected to be slow, uncertain and incomplete.

It has been shown that there is a great variety of substances which act as photosensitizers, not only carbonyl substances, but many halogenated hydrocarbons. Further research would probably increase and widen the list. All these have a dual function. In the absence of oxygen, photosynthesis results; in the presence of oxygen, photolysis, with the production of oxidation products. It does not follow that these will be found to be identical with the oxidation products obtained with catalysts which do not require irradiation, such as cobalt linoleate, copper and other metallic salts, or oxidizing agents such as nitro aromatic com-

pounds. None of these latter acts as photosensitizers; they either retard or prevent gelling on exposure.

It would seem also that the mechanism of photogel formation is quite distinct from vulcanization, even when a vulcanizing agent is employed as a sensitizer. When benzoyl peroxide is used as a vulcanizing agent, a relatively high temperature is necessary, and air must be excluded, that is, rubber milled with benzoyl peroxide may be vulcanized in a mould but not in the open; the latter results in a soft, sticky and half-fluid mass. Gel formation at room temperature in the absence of air, whether in the light or dark, yields a product of different physical properties to that obtained by vulcanization.

An outstanding fact regarding the formation of photogels is the substantial identity in the nature of the products and rate of gelling of different types of rubber, whether crude, purified, milled or raw. If gelling be regarded as merely polymerization, whether by formation of bridges or by actual lengthening of the thread-like molecule, an enhanced result should be obtained by starting with an unmilled rubber. In that case the molecules are initially longer, and any further lengthening or other form of binding should yield stiffer gels than when shorter molecules form the initial units. Also a quicker gelling would be expected. The substantial identity in behavior of raw and milled crepe is evidence that the change is not the result of the formation of either longer threads or cross linking, but rather of new chemical derivatives of rubber.

It is also noteworthy that, to exert an appreciable effect, sensitizers must be present in substantial proportion relative to the rubber. Less than 5 per cent produces a barely appreciable acceleration of gelling, and 1 per cent is a limiting figure. If sensitizers acted as catalysts of gel formation, much smaller quantities should have a noticeable effect. The fact that relatively large quantities are required also favors the view that a chemical reaction with the rubber has taken place.

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# ANALYTICAL METHODS IN RUBBER CHEMISTRY, PART I \*

## GENERAL ANALYTICAL CONSIDERATIONS

E. H. FARMER

### INTRODUCTION

One of the consequences of the high-molecular character of rubber is the smallness of the effect on ultimate quantitative analysis of the presence of one or even several heteroatoms or groups in the long hydrocarbon chains. With rubber molecules possessing an average chain-length of about 4,500 isoprene units, the association of, say, ten nitrogen atoms with each chain would provide a nitrogen content of only about 0.0007 per cent, and the incorporation of about 0.005 per cent of ethereal oxygen in pure rubber hydrocarbon would be theoretically capable of providing sufficient linking material for an infinite degree of heteropolymerization, or, if the oxygen were applied instead to produce the maximum possible degree of degradation, it would be capable of severing from one-quarter to one-third of the rubber chains. In view of these dimensions, and the fact that natural rubber normally contains difficultly removable hetero components, and is ready to take up additional amounts of oxygen, little progress can be made in the fundamental investigation of the complex molecules without a suitably accurate technique of chemical analysis, and this applies particularly to the determination of total oxygen and total nitrogen, and also to the determination of the six types of combined oxygen likely to be present in rubber, *viz.*, hydroxylic, oxido-, ethereal, peroxidic, carbonyl and carboxylic. Unfortunately, great precision in estimation cannot be achieved without increasing greatly the rigour of the analytical technique, and perhaps it is not surprising that Midgley, Henne and Renoll's well-known high-precision method for determining carbon, hydrogen and, by difference, oxygen, still remains after five years the sole such chemical analytical method reported in the literature.

One may recognize, as is usual in organic chemistry, two groups of analytical determinations, ultimate elementary analyses and estimations of functional groups such as hydroxyl or carbonyl. The characteristic properties of rubber hydrocarbon and also of the somewhat modified rubbers are not favorable to the development of high accuracy in ultimate analysis, as the high-molecular character, hydrocarbon structure and restricted solubility all render difficult complete degradation by the usual methods. The most hopeful line of approach seems to be to concentrate on improving those methods which go furthest in the desired direction and have no fundamental disqualifications. In this category is the determination of nitrogen, for which an improved procedure designed to increase the accuracy of the Kjeldahl method is described by Tristram<sup>1</sup>.

In the determination of functional groups, however, *e.g.*, hydroxyl or carbonyl, the principal difficulty is to determine whether the reaction is complete; usually there is no absolute or direct means of testing this. The thousand-fold repetition of the constituent isoprene units of rubber to form pliated chains seems to depress the reactivity of even such intrinsically reactive groups as hydroxyl, whether

\* Reprinted from *Translations of the Institution of the Rubber Industry*, Vol. 16, No. 5, pages 260-275, February 1941.



these groups are distributed here and there along the chains or occur in all or most of the isoprene units. To counter this tendency, it is essential to use reagents of an energetic character, and then to try to determine whether the reaction with the functional groups has been complete. The difference in relative efficiency from reagent to reagent is well exemplified by iodine chloride and molecular hydrogen (the latter in presence of an active catalyst), the one tending towards complete addition at the double bonds under mild conditions, the other never becoming complete, even at high temperatures and pressures, before degradation of the rubber sets in. In the determination of active hydrogen, for which an improved Zerewitinoff procedure suitable for use with rubber or modified rubbers is described by Bolland<sup>2</sup>, the reagent is intensely reactive, so the main difficulty is to eliminate traces of water which cling to glass surfaces and solvents, and engender errors of comparable magnitude to the values to be determined. In determinations of active hydrogen in slightly oxidized rubbers by the ordinary microtechnique, it is not unusual to find that the deduced values for the hydroxylic oxygen present are greatly in excess of the values for total oxygen as determined by careful microanalysis.

## DETERMINATION OF NITROGEN

G. R. TRISTRAM

Much work has been carried out on the fractionation of rubber hydrocarbon<sup>3</sup> and, in connection with this work, it has been necessary to improve existing methods of determining the proportion of heterogeneous components in the hydrocarbon samples. Since nitrogenous material, chiefly protein, is the main impurity in the raw material employed (acetone-extracted crepe, or rubber from trypsin-digested latex), the nitrogen content of the various fractions has been taken as one of the criteria of purity. It was sought to develop a method capable of estimating with satisfactory precision nitrogen contents as low as 0.01 per cent (approximately 0.06 per cent protein); then, for the purposes of the experiments, it seemed reasonable to regard any fraction which contained less than 0.01 per cent nitrogen as composed of nitrogen-free hydrocarbon.

*Choice of method.*—The methods available included those of Dumas and Kjeldahl. The former method may be used, on a microscale, to estimate 0.30 mg. of nitrogen, which, in the extreme case visualized above, would necessitate the combustion of 3.0 grams of rubber. An attempt was made to burn crepe rubber (0.35-0.45 per cent N) on a semimicro scale, but large volumes of an inflammable gas were produced. The copper oxide in the combustion tube was replaced by lead chromate without any improvement, and the method was therefore abandoned. The difficulty seemed to be due to the impossibility of making an intimate mixture of oxidizing agent and rubber hydrocarbon. Attention has therefore been restricted to the Kjeldahl method.

*The micro-Kjeldahl.*—In ordinary circumstances, 10 to 20 mg. of material is digested but, to estimate the nitrogen content of highly purified rubbers, it was necessary to digest increased amount (200-300 mg.) of material. This necessitated the use of a larger volume of acid and of a modified distillation apparatus to accommodate the increase in the volume of the reagents. At the same time it was essential to maintain, or even to increase, the accuracy of the ammonia determination. The essential practical details will be discussed at some length.

*Digestion of the rubber hydrocarbon.*—Special Kjeldahl digestion tubes of 30 cc. capacity were used and, after experimentation, the following procedure

was adopted. The weighed sample of rubber was dropped into 500 volumes of hot sulfuric acid (5 cc. per 100 mg.), for it was found that preheating the acid effectively increased the rate of digestion. When the digestion liquor started to fume, 0.1 to 0.2 gram of catalyst was added, and the reaction was allowed to continue until the solution cleared.

*Choice of catalyst.*—The digestion of increased amounts of material made necessary the use of an efficient catalyst. In the course of the work the following have been tested: copper sulfate, sodium selenate, potassium disulfate, mercuric sulfate, Campbell and Hanna's catalyst<sup>4</sup> consisting of 1 part of  $H_3PO_4$  and 3 parts of  $H_2SO_4$ , and containing 1 per cent  $CuSO_4$  and 1 per cent  $Na_2SeO_4$ , and a mixed catalyst (A) consisting of 15 parts of  $Na_2SO_4$ , 2 parts of  $CuSO_4 \cdot 5H_2O$ , and 1 part of  $Na_2SeO_4$ . A large number of determinations was carried out with each catalyst, and it was found, in general, that the single substances were less efficient than the mixed catalyst (A), which, accordingly, in

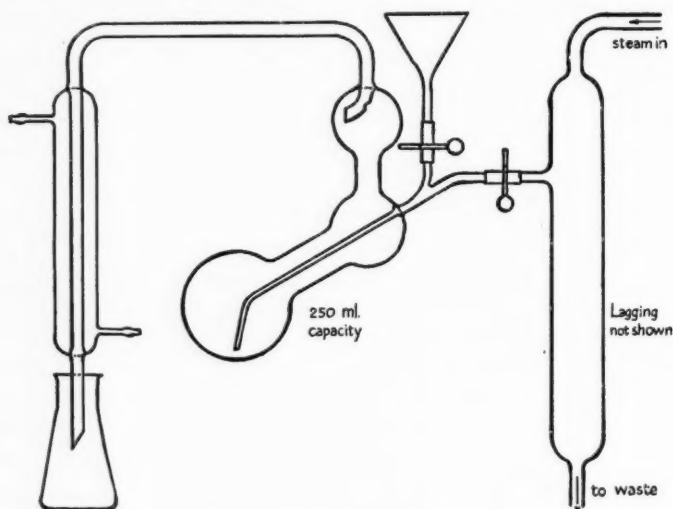


FIG. 1.—Distillation apparatus.

the modified form, was adopted as the standard catalyst. Incidentally it may be noted that sodium selenate has been found to contain nitrate, and it is advisable to test this reagent before using it in the mixture.

*Distillation of ammonia.*—The distillation apparatus was a standard micro-apparatus<sup>5</sup>. The only modification was to enlarge the bulb to 250 cc. capacity. (See Figure 1.)

To keep volumes as low as possible, 40 per cent sodium hydroxide solution was replaced by saturated sodium hydroxide. The water in the steam generator was kept acid to methyl red, chips of pumice being added to promote even boiling.

*Estimation of ammonia.*—The methods available included absorption of ammonia in standard acid, and a Nessler estimation. Only the former method has been utilized in this work, but it has been found that as little as 0.02 mg. of nitrogen produces significant color with Nessler's reagent, although the quantitative estimation of ammonia by colorimetric analysis was difficult.

In the present work,  $N/140$  acid with an internal indicator has been used, and it has been found to give reproducible results with as little as 0.03 mg. of nitro-

gen. Amounts of nitrogen as low as 0.012 mg. have been estimated, but no great accuracy is obtained when the titration is less than 0.3 cc., i.e., 0.03 mg. of nitrogen.

*Preparation of acid and alkali.* (a) *Acid.*—A mixture of 0.72 cc. of 10 *N* hydrochloric acid, 200 cc. of 95 per cent ethyl alcohol and 10 cc. of stock indicator solution is made up to 1 liter with boiled-out distilled water. The stock solution of indicator consists of 250 cc. of alcohol, containing 0.2 gram of methyl red and 0.05 gram of methylene blue, and is permanganate-pink in acid solution, almost colorless when neutral, green in alkaline solution and almost insensitive to carbon dioxide. The acid should be standardized by distillation of ammonium sulfate. A solution containing 2.36 mg. of ammonium sulfate per 5 cc. is suitable for *N*/140 acid.

(b) *Alkali.*—This is prepared by the oily lye method of Sörensen. The alkali, (20 g. NaOH AnalaR) is dissolved in 20 cc. of boiled-out distilled water in a stoppered flask. After being cooled, the flask is immersed in water at 100° for 8 hours. Any insoluble sodium carbonate is removed by filtration through sintered glass, and 0.4 cc. of the lye is then diluted with 900 cc. of boiled-out water. After 24 hours, the alkali is standardized against the acid.

*Precautions.*—Before carrying out each series of estimations, the apparatus should be steamed out for at least 30 minutes. With *N*/140 acid, it is necessary to exclude carbon dioxide. The burettes used by the author were of the reservoir type, the reservoirs being coated internally with paraffin wax; the acid and alkali maintained their strength indefinitely as long as the carbon dioxide absorbing agent (Sofnolite) was not allowed to become spent. In the case of alkali, it is necessary to empty and refill the burette if more than a few hours (maximum 24) elapse between each series of estimations, because the alkali, when in contact with glass, changes strength with astonishing rapidity. A Conway microburette, if available, may be used. This form of burette makes it possible to use increased the strengths of acid and alkali, and thus renders the titration even less susceptible to carbon dioxide.

It is the practice of the author to use as little excess of acid as possible so that the back-titration does not exceed 0.1 cc. of alkali. In this way one need not know the strength of the alkali within 1 to 2 per cent. With such dilutions of ammonia as are here in use, it is not necessary to have an excess of acid in the receiver, because no ammonia is lost if the solution becomes alkaline.

It is recommended that all estimations be carried out at least in duplicate. Where it is necessary to digest amounts of rubber of the order of 200 mg. or where a titration of only 0.2 to 0.5 cc. is expected, triplicate estimations should be made. A blank estimation, using the same amounts of acid, catalyst and alkali (for neutralization) should be made with each series, and on no account should this exceed 0.04 cc. of acid.

The method has been checked repeatedly against standard solutions of ammonium sulfate. The results of these experiments are recorded in Table I.

It can be seen that the recovery of nitrogen over the whole range of 0.66 to 0.013 mg. is good, but that, below about 0.05 mg., recovery becomes dependent on the accuracy of titration and on the constancy of the blank. In all the analyses made on rubber, it has been the aim to ensure a titration of at least 0.3 cc. of acid.

*The validity of the Kjeldahl method.*—Although it has been impossible to check the analysis of rubber by direct combustion, there is no reason to suppose that

the Kjeldahl method does not give maximum values; indeed, during the present work evidence has been obtained which lends support to this view. Thus:

(1) A large number of estimations have been carried out, using nine different catalysts, some of which contained salicylic acid or glucose to fix any nitro groups. With crepe rubber (N, 0.33 per cent) and trypsin-purified rubber (N, 0.05 per cent), the nitrogen content found was not altered by changing the catalyst.

(2) In fractionation experiments it was found that the sum of the nitrogen contents of the fractions was equal to the nitrogen content of the original material.

(3) In the end-fractions obtained by Bloomfield and Farmer<sup>3</sup>, the carefully determined carbon and hydrogen values would not allow of more nitrogen than was found by Kjeldahl determinations.

(4) A sample of protein (edestin 18.55 per cent N; tyrosine 4.31 per cent N) was milled into nitrogen-free rubber (trypsin-digested). The nitrogen content of the mixture was 2.70 per cent; the tyrosine content 0.63 per cent. These values

TABLE I  
RECOVERY OF NITROGEN

Nitrogen (mg.)	Titre	Nitrogen found (mg.)	Recovery (per cent)
—	0.04	—	—
0.560	6.04	0.66	100
0.514	5.18	0.514	100
0.277	2.78	0.274	99.0
0.257	2.64	0.260	101.1
0.250	2.53	0.249	99.6
0.10	1.04	0.10	100
0.10	1.04	0.10	100
0.077	0.82	0.078	101.3
0.050	0.53	0.049	98.0
0.051	0.57	0.053	103.9
0.050	0.55	0.051	102.0
0.0257	0.29	0.025	97.4
0.013	0.17	0.013	100
0.013	0.18	0.014	107.8
0.013	0.18	0.014	107.8

correspond to a protein content of 14.58 per cent and 14.62 per cent, respectively. As tyrosine may be estimated with an accuracy of 1 per cent, and is not influenced by the presence of impurity<sup>6</sup>, it is clear that in this case, at any rate, the nitrogen content has been determined accurately by the Kjeldahl method.

Some typical analyses which have been made on various samples of rubber hydrocarbon are recorded in Table II.

#### SUMMARY

The application of the Kjeldahl method to the determination of nitrogen in rubber has been studied in detail.

By a suitable combination of the macro- and micromethods, as little as 0.025 mg. of nitrogen has been estimated with considerable accuracy, and the presence of as little as 0.0143 mg. has been detected.

Various catalysts have been tried, and a mixed catalyst containing sodium sulfate, copper sulfate and sodium selenate is recommended for general use.

Evidence has been obtained of the validity of the results obtained by the Kjeldahl method.

TABLE II  
NITROGEN IN RUBBER HYDROCARBONS

Sample	Weight digested (mg.)	Titre (cc.) (Blank 0.04 subtracted)	Nitrogen (per cent)
Crepe rubber 1.....	143.1	4.56	0.32
Crepe rubber 1.....	88.0	2.74	0.31
Crepe rubber 1.....	34.9	1.23	0.35
Crepe rubber 1.....	Mean of 14 additional determinations		0.33±0.02
Low-nitrogen rubber .....	111.1	0.54	0.05
Low-nitrogen rubber .....	85.3	0.43	0.05
Low-nitrogen rubber .....	112.6	0.56	0.05
Low-nitrogen rubber .....	114.9	0.57	0.05
Trypsin-purified 1 .....	272.9	1.17	0.04
Trypsin-purified 1 .....	297.6	1.27	0.04
Trypsin-purified 2 .....	260.7	0.38	0.015
Trypsin-purified 2 .....	296.4	0.42	0.014
Sol rubber .....	290.0	0.29	0.010
Sol rubber .....	296.4	0.35	0.012
Gel rubber .....	55.0	4.68	0.85
Gel rubber .....	57.5	4.76	0.83
Crepe rubber 2.....	156.6	6.62	0.42
Crepe rubber 2.....	196.4	8.11	0.41
Crepe rubber 2.....	95.6	3.90	0.41
Crepe rubber 2.....	84.5	3.45	0.41

## DETERMINATION OF ACTIVE HYDROGEN

J. L. BOLLAND

In the course of an investigation into the mechanism of oxidation of rubber, it was found essential to analyze certain oxidation products for small proportions of hydroxyl. Although it has been conclusively demonstrated by several authors<sup>7</sup> that the original Zerewitinoff method of analysis may be adapted successfully on the micro- and macroscales to determine the active hydrogen content of relatively simple organic substances, with some accuracy, the problem of dealing with difficultly soluble substances, such as rubber derivatives, remains. The modified technique here described surmounts the difficulty, and the adoption, for the purpose of carrying out the analysis, of an apparatus designed to operate under high-vacuum conditions increases considerably the precision of the method. The latter aspect is especially important when dealing with substances of low active hydrogen content and limited solubility. The following general procedure has been found to give satisfactory results, judged by the reproducibility of analyses on rubberlike substances, and the accuracy with which the active hydrogen content of certain definite long-chain molecules can be determined.

**General procedure.**—The sample of the substance to be analyzed is dissolved in a suitable solvent, under conditions which rigidly exclude moisture, and then transferred to the actual analytical apparatus. In the latter the sample is brought into contact, *in vacuo*, with an excess of Grignard reagent, and the methane formed, confined in a system of known volume, is determined accurately by measuring its pressure by a McLeod gauge.

In virtue of precautions taken in preparing the solution of the material to be determined and of pretreatment of the reagent designed to eliminate adventitious traces of moisture or methane-forming impurity before interaction takes place, it is possible to reduce the total amount of methane arising from



sources other than the sample to a low, yet reproducible, value. As this total blank may normally be reduced to about  $0.10 \times 10^{-5}$  moles of methane, it is possible to obtain accurate results with a sample containing only  $2 \times 10^{-5}$  gram-atoms of active hydrogen.

*Preparation of Grignard reagent.*—The most suitable Grignard reagent for the present purpose appears to be a solution of methyl magnesium iodide in xylene, although toluene, anisole and isoamyl ether have been used successfully as solvents.

The reagent is conveniently prepared by the interaction of magnesium (2 grams) with methyl iodide (5 cc.) in ethyl ether. The ether is then distilled off *in vacuo*, the final traces being removed by evaporation into a tube, cooled in liquid air, maintained at  $10^{-3}$  mm. permanent gas pressure for some considerable time. Xylene (100 cc.) is next introduced, after filling the flask with nitrogen. The reagent is then pipetted in 10-cc. portions into well dried ampoules, which are sealed off under nitrogen and kept for later use. With the suggested quantities, a saturated solution of approximately 0.7N strength is obtained.

*Preparation of solutions.*—Two methods of preparing thoroughly dry solutions of the material to be determined have been tried with success. The first, in which the solvent is purified by distillation from a quantity of Grignard reagent, is the more rigorous, but is somewhat more laborious. The apparatus required (Figure 1 (a)), after being cleaned with chromic acid solution, is thoroughly dried by attachment at A to the main vacuum line, in which an ultimate pressure of  $10^{-5}$  mm. of mercury may be maintained by means of a two-stage mercury diffusion pump, backed by a rotary oil pump. During the drying operation the apparatus should be well flamed. The apparatus is then opened at C, the sample introduced either in the form of a measured volume of solution of known concentration, or as a weighed amount in a small glass capsule. The apparatus is sealed off at D, and the bulk of solvent removed by careful pumping. The last traces of solvent are conveniently removed by application of liquid air to B for several hours; B is then sealed off at the constriction provided. The solvent (about 5 cc.), usually toluene which has been previously dried by phosphorus pentoxide and a small quantity (about 1 cc.) of Grignard reagent is pipetted into H after breaking tube G at E. The tube is resealed at F and the apparatus thoroughly evacuated, care being taken to remove any gas from the liquid in H. This is accomplished by warming H to room temperature (with the apparatus cut off from the pumps) and pumping off the gas so liberated after replacing the liquid air bath round H. After heating H at  $45^{\circ}$  C for about 10 minutes, toluene is distilled on to the sample by application of liquid air to tube J. Any possibility of mechanical transfer is prevented by the trap interposed between the tubes. When sufficient solvent has been transferred, tube J is sealed off at L, and shaken mechanically until dissolution of the sample is complete.

The second method of preparing a solution is as follows: A tube of the simple type indicated in Figure 1 (b) is thoroughly cleaned, and then dried by flaming, with the pressure reduced to  $10^{-5}$  mm. pressure, before introduction of the sample. After thorough removal of moisture and solvent (if any) from this receptacle by distillation into a liquid-air trap, the requisite volume of solvent dried with phosphoric oxide is introduced and the tube again evacuated. The earlier stages of this final evacuation should be carried out without the application of liquid air. The tube is finally sealed off at the constriction and shaken to complete dissolution of the sample.

*Reaction vessel.*—A suitable form of Pyrex apparatus, consisting of reaction vessel and McLeod gauge, is shown in Figure 2. The cross-section of the compres-



sion capillary in the McLeod gauge is so chosen that the maximum reading corresponds to about  $2 \times 10^{-5}$  moles of gas contained in the apparatus illustrated.

*Method of analysis.*—The reaction vessel is thoroughly cleaned by treatment with chromic acid, washed with distilled water, and attached to the apparatus at ground-glass joint B. Thorough drying is effected by evacuating for at least three hours, the reaction vessel being flamed at intervals. After admitting air to the reaction vessel through a calcium chloride tube, about 1 cc. of Grignard

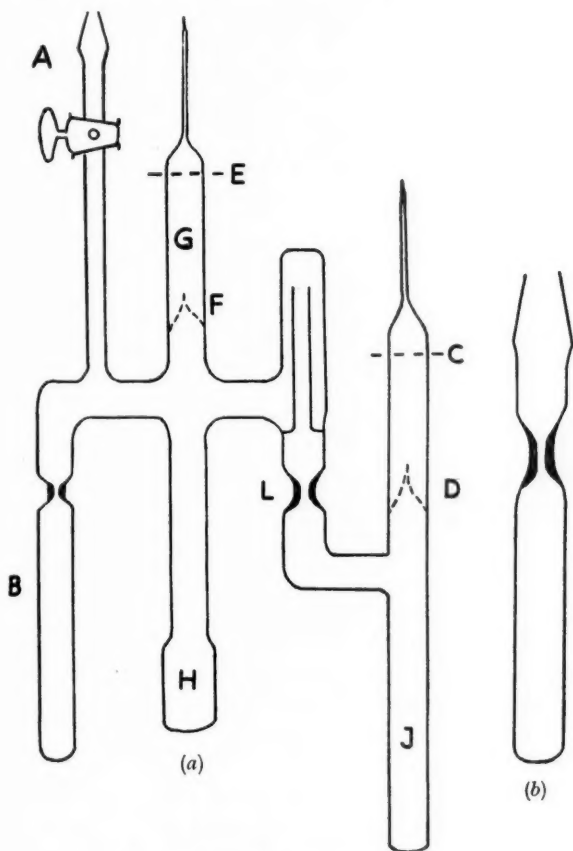


FIG. 1.—Apparatus for drying solvent.

reagent is pipetted into the bottom of tube C through detachable cap D, and a small measured volume (1-3 cc.) of the already prepared solution of the substance to be analyzed (sufficient to give about  $2 \times 10^{-5}$  moles of methane on reaction) is introduced into tube E. The pipettes used for this purpose are protected by a 10-cm. column of finely granulated calcium chloride, and are cleaned before use by flaming them for a few minutes while a stream of dry air is passed through. By weighing tube J (Figure 1) before removal of solution from it, and also the two empty glass fragments obtained by opening it, the concentration of the solution, and hence the weight of sample taken for analysis,

can be determined. The reaction vessel is then evacuated, the solution and reagent being retained by application of liquid air to the two limbs.

The Grignard reagent is then subjected to a treatment designed to remove any impurities which would give rise to methane at the temperature of  $45^{\circ}\text{C}$ , at which the reaction is subsequently to be carried out. Accordingly, tube C is heated for 5 minutes by application of a thermos flask containing water at  $45^{\circ}\text{C}$ . A strip of cotton-wool, thoroughly soaked in tap water, is wound around the tubing connecting C and E and C and B, to prevent undue transfer of

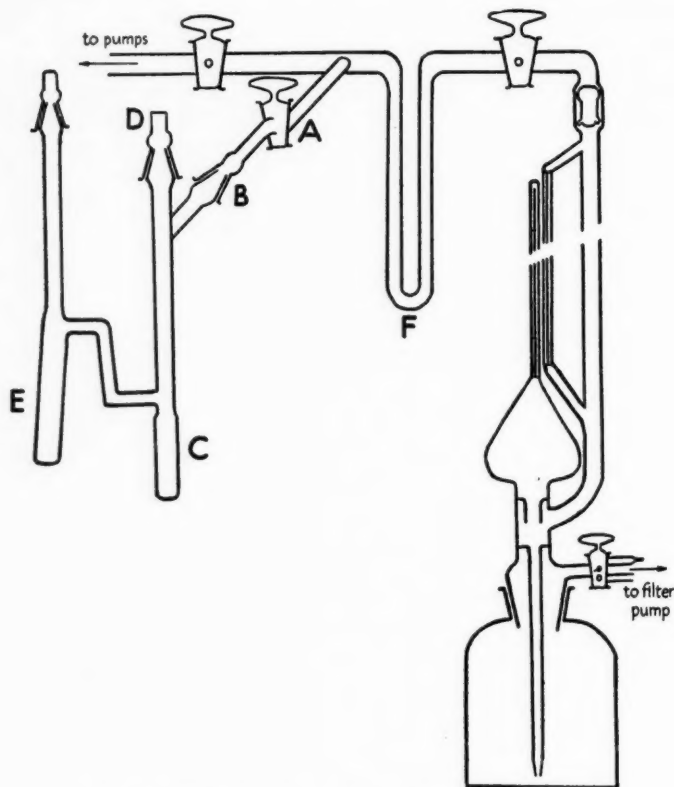


FIG. 2.—Vacuum apparatus with reaction tube in position.

solvent from C. The methane produced by this treatment is readily determined by applying liquid air to C and E for two minutes, and then expanding the gas into the McLeod gauge through the U-tube F, which is kept immersed in liquid air. After the measurement has been completed, the whole apparatus is pumped out (3 min.), the liquids are warmed, and the heating, expansion of gas and measurement repeated. This cycle, consisting of heating, expansion and measurement, is repeated until a 5-minute heating period produces a sufficiently small evolution of methane, the amount so tolerated being about  $5 \times 10^{-7}$  moles, as experience has shown that further repetition of the heating process beyond this point does not readily improve on this figure. If the solvent containing the Grignard reagent is xylene, it is permissible, to carry out the first two heating

periods at 65° C. After such treatment, the amount of methane subsequently produced at 45° C is generally reduced almost to the tolerated value. With lower-boiling solvents than xylene, such as toluene and anisole, this modification of the procedure cannot be employed.

The cotton-wool is then removed from the connecting tube and the reagent and solution are mixed by rotating the reaction vessel in its own plane round ground glass-joint B until reagent flows from C to E. The mixture is heated at 45° C for five minutes, and the methane formed isolated by application of liquid air to C and E. This gas is then expanded into the McLeod gauge, and the pressure is measured; afterwards the apparatus, except for the reaction vessel, is pumped out. The liquid in the reaction vessel is melted and refrozen, and again the pressure obtained by expansion of gas into the McLeod gauge is measured. This cycle is repeated (all the apparatus except the reaction vessel being pumped out after each measurement of pressure) until the pressure generated is reduced to a value comparable to the final reagent blank. In this way the methane remaining dissolved in the reaction mixture is allowed for. It may sometimes be found that heating for five minutes is insufficient to complete the reaction; in such cases the five-minutes' heating-period is repeated. Experience has shown that the end-point in the case of oxidized rubbers can be judged readily, as by interaction between the reagent and sample a yellow gel is formed, the color of which gradually fades as the reaction proceeds, and completely disappears only when the reaction is complete. With simple substances, a five-minute period is sufficient.

For general convenience in active hydrogen determinations, provision is made for the attachment of two similar reaction vessels to the pressure-measuring apparatus. Two analyses may then be performed simultaneously, either duplicates in which successive portions from the same solution are used, or single analyses of two distinct samples.

*Corrections.*—The measured amount of methane, calculated from the pressure measurements and the known volume of the apparatus, must be corrected to compensate, first, for the reagent "blank" caused by heating the reagent to 45° C for five minutes, and secondly, for the solvent "blank," arising from hydroxylic or other objectionable impurities in the solvent in which the sample is dissolved. Blank experiments, in which the active hydrogen content of different amounts of solvent, purified by distillation from Grignard reagent, had been determined, show that the correction to be applied may, in the case of toluene, be expressed in the form:

$$M_s = (0.02 + 0.05 \times v) \times 10^{-5} \text{ moles,} \dots \dots \dots (1)$$

where  $v$  is the volume of toluene used. The numerical data on which this equation is based are given in Table I.

TABLE I

Vol. of solvent (cc.).....	5.0	3.5	2.0	2.0	1.0	—	—
Moles $\text{CH}_4 \times 10^5$ .....	0.31	0.22	0.14	0.11	0.078	0.020	0.030

The low value of the blank, corresponding to absence of solvent, shows that the precautions taken to dry the apparatus were satisfactorily efficient, and that no moisture was introduced during the operations of transferring the solution from the tube in which it was prepared to the reaction vessel.

Samples of toluene, dried by phosphoric oxide, when pipetted directly from the stock-bottle, gave blank values of the same order as the toluene purified by

the more rigid method described above (see Table II); this figure was not appreciably increased by submitting the same toluene to the treatment described in the second method of preparing a solution (see Table II). It must therefore be supposed that this simpler technique is adequate in the case of toluene, even if somewhat less rigorous and certain; on the other hand, the blank arising from anisole dried by phosphoric oxide is rather large, and pretreatment of this particular solvent with Grignard reagent is to be recommended.

TABLE II

Source of toluene	cc.	Moles CH <sub>4</sub> × 10 <sup>3</sup>	Moles CH <sub>4</sub> per cc. × 10 <sup>3</sup>
P <sub>2</sub> O <sub>5</sub> -dried from bottle.....	2.40	19.7	8.2
	2.80	15.9	5.7
	2.40	13.2	5.5
	2.80	15.9	5.7
P <sub>2</sub> O <sub>5</sub> -dried, and treated as in second method of preparing solution	2.90	19.7	6.8
	2.90	22.4	7.7
	2.00	14.0	7.0
	2.50	20.1	8.0

The application of these corrections is exemplified by the following typical example:

*Example.*—The data obtained experimentally were:

- Wt. of total sample (rubber oxidation product) .. = 34.0 mg.  
 Wt. of solvent (toluene) ..... = 3.00 g.  
 Volume of solution taken ..... = 1.10 cc.  
 Therefore wt. of sample taken ..... = 10.78 mg.  
 McLeod gauge readings:  
 (a) Pretreatment of reagent: 84.0\*, 59.0\*, 40.5\*, 34.0\*,  
 32.5\* mm.  
 (b) After reaction: 171.5\*, 100.0\*, 65.0, 40.5 mm.

The characteristics of the apparatus were:

Volume = 200 cc.;  $p = 4.20 \times 10^{-5} h^2$ , where  $p$  is the pressure (mm. of mercury) corresponding to a reading of  $h$  mm. on the McLeod gauge.

Then, pressure of methane:

From pretreatment: 0.296, 0.146, 0.069, 0.048, 0.045 mm.  
 After reaction: 1.238, 0.420, 0.177, 0.069 mm.

and total pressure arising from reaction mixture = 1.904 mm. of Hg; also, pressure arising from reagent =  $2 \times 0.045 = 0.09$  mm. of Hg. Therefore moles of methane from the solution:

$$= \frac{1.81}{760} \times \frac{200}{22400} \times \frac{273}{291} = 2.00 \times 10^{-5}$$

Moles of methane from solvent (equation (1)) =  $0.075 \times 10^{-5}$ . Therefore active hydrogen content of sample:

$$= \frac{1.93 \times 10^{-5} \times 1}{0.0108} \times 100 = 0.179 \text{ per cent}$$

\* After heating for five minutes at 45° C.

*Analysis of standard substances.*—In Table III are included determinations made on substances of known molecular structure, in which the length of hydrocarbon chain corresponding to each active group makes some approach to the proportion in the rubber oxidation-products which it is the present purpose to analyze. Duplicate determinations made with the same solution are indicated by brackets, and the fact that the solution was made by the simpler second method, by an asterisk.

TABLE III

Substance	mg.	Moles of CH formed $\times 10^5$	Active hydrogen (found per cent)	Active hydro- gen (calcu- lated per cent)
Long-chain saturated acid	7.60	2.62	0.345	0.362
	7.00	2.48	0.355	
	4.10	1.45	0.350	
	4.00	1.40	0.354	
	1.21	0.446	0.369	
	1.22	0.461	0.378	
	1.26	0.484	0.383	
	6.01	2.15	0.359	
	6.01	2.21	0.367	
	6.64	2.95	0.444	
Dihydroxytetrahydrosqualene	6.14	2.68	0.435	0.448
	3.81	1.73	0.455	
	3.95	1.85	0.467	

TABLE IV

Weight of sample (mg.)	Moles CH <sub>4</sub> formed $\times 10^5$	Active Hydrogen found (per cent)
43.0	0.39	0.0091
66.3	0.57	0.0086
42.3	1.09	0.0258
42.3	1.06	0.0250
33.6	1.90	0.0565
50.7	3.00	0.0590
23.4	1.99	0.0851
24.2	2.05	0.0847
6.23	2.14	0.344
6.23	2.10	0.337

The long-chain saturated acid mentioned in Table III was supplied by G. R. Tristram, and consisted of a mixture of stearic and palmitic acids derived from dried latex. The calculated active-hydrogen content is based on the carefully determined equivalent weight of the mixed acids. The equivalent weight was 275. The dihydroxytetrahydrosqualene was a polyisoprenic 1:6-glycol, of the formula  $\text{H}(\text{C}_5\text{H}_8)_2 \cdot \text{CH}_2 \cdot \text{CMe}(\text{OH}) \cdot (\text{CH}_2)_4 \cdot \text{CMe}(\text{OH}) \cdot \text{CH}_2 \cdot (\text{C}_5\text{H}_8)_2\text{H}$ , and was supplied by D. A. Sutton.

This series of results suggests that the error of analysis is certainly within 5 per cent, provided a sufficient quantity of methane is measured. This error would doubtless be reduced further if larger samples of the hydroxylic material were used; in such a case the only modification to the apparatus would be an increase of the volume, by the addition of a subsidiary bulb of known capacity, into which the methane is expanded for measurement.

That the reproducibility of results from simultaneous determinations indicated in Table III is also found in the case of rubber derivatives is shown in Table IV, where a few typical analyses of rubber derivatives are recorded.

The author's thanks are due to G. Gee for his continual interest and helpful criticism.

The above work has been carried out as part of the program of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

#### REFERENCES

- <sup>1</sup> See following section, entitled "Determination of Nitrogen", by G. R. Tristram.
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# DISTRIBUTION OF NON-RUBBER SUBSTANCES IN PRESERVED LATEX \*

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The properties of latex depend, not only on its chemical components, but also on the distribution of these components between the rubber and aqueous phases and at the boundary between them. Therefore, to appreciate the function of different components in affecting the behavior of latex, it is necessary not only to know their nature and quantity, but also how they are distributed. For example, a component dispersed in the aqueous phase is not likely to affect coagulation or stability in the same way as the same substance concentrated in the boundary between rubber globules and water. Moreover, a component dissolved in the rubber phase is not likely to have marked effects on the properties of the liquid latex, although it may be of considerable technical importance when the rubber phase has been separated and dried.

This paper records experiments made to obtain a satisfactory technique for measuring the distribution of the non-rubber substances in latex; its application in particular to nitrogen, acetone- and alcohol-soluble substances, water-soluble acids and long-chain fat acids; the influence of various factors such as particle size, dilution, pH, the addition of alkalies, enzymes, soaps, storage in the dark; finally, conclusions are drawn relating to the composition of the boundary layer between rubber and serum and of the interior of the rubber globule.

*Method of determination.*—The general principle underlying the method is simple, and consists in determining the amount of serum substance present in latex as a whole and in the aqueous phase alone, the difference between the two values giving the amount of substance concentrated in the rubber phase and at the rubber-water interface. The development of the method will be illustrated with reference to the distribution of nitrogen, this being selected as the most important value for study on account of the dependence of latex on protein for its stability. Total nitrogen in the latex was determined by the Kjeldahl method on films dried in air and kept in a desiccator, and nitrogen in the aqueous phase on portions of clear serum dried over a boiling water bath. Ammonia of preservation is thus not included in either of these determinations. The investigation was conducted on ammonia-preserved latex and on latex preserved with sodium pentachlorophenate.

The calculation of nitrogen associated with the rubber,  $N_r$ , is made in the following manner:

Let  $S_t$  = Total solids in latex (per cent latex)

$S_w$  = Total solids in aqueous phase (per cent water)

$N_t$  = Total nitrogen in latex (per cent latex)

$N_w$  = Total nitrogen in aqueous phase (per cent water)

$N_r$  = Nitrogen associated with rubber phase (per cent rubber)

$$\text{then } N_r = \frac{N_t - N_w \left( 1 - \frac{S_t}{100} \right)}{S_t - S_w \left( 1 - \frac{S_t}{100} \right)} \cdot 100$$

\* Reprinted from *Transactions of the Institution of the Rubber Industry*, Vol. 16, No. 4, pages 165-183, December 1940.

The successful operation of the method depends on whether it is possible to obtain serum free from rubber without disturbing the existing distribution of non-rubber substances. Three methods have been tried, namely, filtration, centrifuging and creaming.

In the case of filtration, using porous battery jars or a Bechhold porcelain ultra-filter, complete separation of serum from rubber was difficult to obtain at concentrations of rubber above 20 per cent. In addition, irregular results were obtained, presumably due to nitrogenous material being entrapped by the paste which tended to form on the walls of the filter.

Separation of latex into cream and skim fractions was carried out in a laboratory centrifuge in specially designed tubes fitted with ground glass stoppers to prevent evaporation and taps for the withdrawal of serum. As the particles in latex are not uniform in size  $N_r$  values calculated by the centrifuge method can be accurate only when the skim approaches the rubber-free condition.

A more convenient method for separating rubber from serum is by means of creaming agents. The amount of material required to obtain a rubber-free underlayer is small, and separation occurs in a few hours. It is not necessary to wait for equilibrium to be established before sampling the underlayer, as it is found that the composition remains constant throughout the separation. When nitrogen analyses are being conducted, it is desirable to use a material containing no nitrogen, such as methyl- or glycolcellulose or sodium alginate. Most natural creaming agents, such as tragon seed gum and gum tragacanth, contain appreciable amounts of nitrogen. Manucol brand of sodium alginate is made in two grades of low and medium viscosity and both have been found to be satisfactory for the purposes of these experiments. Nitrogen in Manucol was estimated at 0.02 per cent, so that the nitrogen added to the latex when using this creaming agent is only about 0.00002 per cent.

To test whether the existing equilibrium between serum nitrogen and nitrogen associated with the rubber is altered by the addition of creaming agent, an experiment was made in which latex, from which the sludge had been removed by allowing it to settle, was allowed to cream in the presence of sodium alginate so that a rubber-free underlayer was obtained, and a further portion of the same latex was centrifuged until the skim contained less than 0.4 per cent rubber. The following results were obtained:

by centrifuging:	$N_w = 0.124$ per cent
	$N_r = 0.154$ per cent
by creaming:	$N_w = 0.125$ per cent
	$N_r = 0.150$ per cent

The close agreement between the two sets of results shows that the addition of creaming agent does not alter the distribution of the protein between rubber globules and water. This conclusion is supported by the experimental results of Bondy<sup>1</sup>, which showed that sodium alginate was only weakly adsorbed at the surface of rubber globules in latex. Methylcellulose, however, is comparatively strongly adsorbed, and for this reason, as Bondy points out, it must be displaced from the rubber-water interphase by means of a more surface-active material, such as soap, before the globules can adhere. Apart from the possibility that methylcellulose may alter the distribution of serum substances in latex, it is by no means so efficient a creaming agent as sodium alginate and its use in distribution experiments is not recommended.

*Application of the method to nitrogen distribution.*—Some typical data for

nitrogen distributions in different types of latex are given in Table I. They show that the amount of nitrogen associated with the rubber ( $N_r$ ) varies considerably among the samples, and that this variation is not obviously dependent on the method of preparation, although the centrifuged samples tend to have lower values than the others. The variation in the amount of nitrogen associated with the aqueous phase ( $N_w$ ) naturally depends on the method of preparation (removal of serum substances, concentration, etc.). There is no obvious con-

TABLE I

Sample	Description	Concentration of rubber phase	$N_w$ (Per cent)	$N_r$ (Per cent)
		$S_t - S_w \left( 1 - \frac{S_t}{100} \right)$ (Per cent latex)		
A	40 per cent ammonia latex.....	23.61	0.184	0.159
B	40 per cent ammonia latex.....	16.17	0.099	0.180
C	40 per cent ammonia latex.....	19.58	0.143	0.146
D	40 per cent ammonia latex.....	19.19	0.131	0.111
E	40 per cent ammonia latex.....	32.28	0.266	0.158
F	Creamed concentrate .....	24.87	0.078	0.200
G	Creamed concentrate .....	19.85	0.066	0.131
H	Centrifuged concentrate .....	24.99	0.082	0.133
J	Centrifuged concentrate .....	19.96	0.056	0.096
K	40 per cent latex preserved with 0.9 per cent sodium penta- chlorophenate .....	16.90	0.088	0.182
L	Creamed concentrate preserved with 0.1 per cent ammonia and 0.3 per cent sodium penta- chlorophenate .....	24.14	0.069	0.167

TABLE II

Latex	Type	Age (mos.)	NH <sub>3</sub> (Per cent)	No. of cream- ings	Final pH	Rubber phase (Per cent)	$N_w$		$N_r$		$N$ per cent in crepe from final cream
							Initial (Per cent)	Final (Per cent)	Initial (Per cent)	Final (Per cent)	
P	40 per cent.. ammonia- preserved	6	0.6	10	9.5	27.5	0.208	0.0016	0.173	0.131	0.126
Q	40 per cent.. ammonia- preserved	15	0.5	7	6.5	25.1	0.198	0.0036	0.135	0.134	0.147
R	40 per cent.. ammonia- preserved	15	0.8	7	6.5	24.8	0.194	0.0027	0.108	0.100	0.114

nection between  $N_w$  and  $N_r$ . In field latex  $N_r$  amounts to about 25 per cent of the total nitrogen, but in purified latices the proportion is much higher.

The effect of different variables on the nitrogen distribution will now be considered.

*Dilution.*—The effect of dilution was studied by a technique which involved repeated creaming of latex by successive removals of underlayer and replacement with creaming agent solution. The final values for  $N_r$  were checked by crepeing the purified coagulated creams and determining their nitrogen contents; fair agreement was obtained between the two sets of results. The data given in Table II show that dilution removes only a fraction of the surface

nitrogen from the rubber globules, that the ease of removal is probably determined by the pH of the latex, and that old ammoniated latex (*Q* and *R*) has less surface nitrogen than commercial ammoniated latex of good color.

In the experiment with latex *P*, ammonia was added at intervals, so the pH value never fell below 9.5. The results showed that some desorption of protein occurred, since, although the serum solids were diluted over a thousand fold,  $N_w$  fell only to one-one hundred and thirtieth of its original value, and the final value of  $N_r$  was 76 per cent of the initial value. The results appeared to be adequately represented by the equation:  $N_r = 0.128 N_w^{0.056}$ , which is of the type

$\frac{x}{m} = K.C^{\frac{1}{n}}$ , proposed by Freundlich on empirical grounds to cover adsorption

equilibria of the liquid-solid type. The value of  $\frac{1}{n}$  usually lies between 0.1 and 0.7, so adsorption of protein on rubber is considerably stronger than that of liquids on porous adsorbates, such as charcoal or silica gel. The data obtained on latices *Q* and *R* show that under some conditions, *e.g.*, lower pH, protein is

TABLE III

Description of latex	Original d.r.c. (Per cent)	Series I			Original d.r.c. (Per cent)	Series II		
		$N_w$ (Per cent)	$N_r$ (Per cent)	Relative average particle diameter		$N_w$ (Per cent)	$N_r$ (Per cent)	Relative average particle diameter
Parent latex . . . . .	38.3	0.184	0.159	2.03	38.0	0.143	0.146	1.56
Centrifugal cream. . . . .	60.3	0.082	0.133	2.50	62.6	0.056	0.096	2.59
Centrifugal skim. . . . .	—	—	—	—	26.0	0.320	0.215	1.01
Centrifugal skim re-centrifuged . . . . .	50.5	0.122	0.212	1.47	—	—	—	—
Centrifugal skim creamed . . . . .	36.1	0.230	0.302	1.00	53.9	0.079	0.217	1.00
Parent latex creamed . . . . .	—	—	—	—	57.7	0.066	0.131	1.77

even more difficult to remove. After two creamings, the surface nitrogen in latex *Q* increased from 0.135 to 0.147 per cent, perhaps due to reduction in pH, but subsequent creamings caused a steady removal to just below the initial figure. In both these cases no attempt was made to maintain the pH at a fixed value, in view of the fact that maximum spreading of proteins sometimes occurs at the isoelectric point<sup>2</sup>.

As a matter of interest, the following additional data obtained on purified cream from latex *P* are recorded. Total solids 45.39 per cent, dry rubber content 45.24 per cent; acetone extract 2.19 per cent (original crepe 3.07 per cent); acid value of acetone extract 142 mg. potassium hydroxide per 100 g. of crepe (original value 234 mg. potassium hydroxide).

*Particle size.*—Two parent latices were separated by the Rubber Research Scheme, Ceylon, into fractions containing rubber particles of different size, by centrifuging and creaming.

The results of  $N_r$  and  $N_w$  determinations are given in Table III. Those on series I were made at a dry rubber content of 25 per cent and on series II at 20 per cent.

As  $N$  is measured in terms of mass, and small particles have a larger surface per unit of mass than big particles,  $N$  should increase in the following order, for

different fractions of the same parent latex: centrifugal concentrate, creamed concentrate, parent latex, namely centrifugal skim recentrifuged, and the highest value of all should be given equally by centrifugal skim or centrifugal skim creamed. It will be seen that the values given in Table III do, in fact, follow this order, and that in series II the values for centrifugal skim and creamed centrifugal skim are identical within experimental errors. It will be shown later that about 0.02 per cent of the  $N_r$  value (calculated on the rubber) is firmly bound, and that the remainder resides at the rubber-serum interface.  $N_r$  (less 0.02 per cent) therefore represents a surface property of the rubber.

If it is assumed that surface concentration of nitrogen is the same for large and small particles in the same parent latex, it can be calculated that the relative average particle size  $\left(\frac{\sum nd^3}{\sum nd^2}\right)$  for the above latex is as given in columns 5 and 9 of Table III, where  $n$  is the number of particles of diameter  $d$ . It will be seen that the particles in the centrifuged concentrate are about 2.5 times the diameter of those in the skim.

*Enzymes.*—Experiments with proteolytic enzymes were carried out as part of an investigation on the purification of latex, in the course of which data relating to the effect of enzymes on nitrogen distribution were obtained.

TABLE IV

Temp. of enzyme (° C)	$N_r$ Control (Per cent)	$N_r$ Pepsin (Per cent)	$N_r$ Trypsin (Per cent)	$N_r$ Papain (Per cent)
30	0.197	0.171	0.107	0.175
40	0.166	0.144	0.111	0.167
60	0.162	0.178	0.123	0.103
68	0.152	—	—	0.124

A comparative study of the enzymes: trypsin, pepsin and papain was made at 30° C, 40° C and 60° C, and of papain at 68° C, the papain being activated with potassium cyanide. 300 cc. portions of latex containing 31.5 per cent total solids, 29.6 per cent dry rubber content and 0.85 per cent ammonia were treated with 1.2 grams of enzyme in 30 cc. of water (in the case of papain 0.2 gram of potassium cyanide was first dissolved in the 30 cc. of water) and the latices were stored for 24 hours at 30° C, 40° C and 60° C, and the papain-treated latex also for 24 hours at 68° C. The latices were then creamed at room temperature with tragon seed gum to determine the nitrogen in the aqueous phase. The analytical data were corrected for nitrogen in the enzymes, creaming agent, and potassium cyanide; the calculated values of  $N_r$  are given in Table IV.

The results show that decomposition of the protein by enzymes is accompanied by a reduction in the amount of nitrogen associated with the rubber. None of the enzymes caused complete removal of protein nitrogen, but trypsin reduced the amount adsorbed by nearly one-half at 30° C, and about one-third at 40° C. Papain is most active at temperatures above the optimum for other enzymes, and the results indicate that it is most active in preserved latex at 60° C. Pepsin is usually most active in acid conditions, and the results indicate that this enzyme has only a small effect on ammonia-preserved latex. The results show also that heating at temperatures above atmospheric without enzyme, but in the presence of ammonia, causes a diminution in the protein attached to the rubber.

The purified creams from the most successful treatments were coagulated after dilution, soaked in distilled water for 20 hours, creped and air-dried for three



weeks. Nitrogen determinations gave the following results: control crepe at 30° C, 0.22 per cent; trypsin at 30° C, 0.094 per cent; trypsin at 40° C, 0.099 per cent; papain at 68° C, 0.094 per cent. A comparison of these figures with  $N_r$  values suggests that part of the nitrogen remaining attached to the rubber was removed on coagulation and crepeing when the latex cream had previously been treated with an enzyme, but that coagulation of the control latex cream resulted in an increase in the nitrogen coagulated with the rubber.

It appears from these investigations that trypsin at 30° C and papain at 60° C are both equally effective in hydrolyzing proteins in latex and that the decomposition affects the distribution of nitrogen so that less of it is adsorbed by rubber. It follows, therefore, that these enzymes facilitate the purification of rubber by dilution, soaking or washing. Pepsin is usually active in acid solution, and it is not surprising that it has little effect on ammonia-preserved latex.

*Caustic alkalis.*—Caustic soda renders the proteins in latex soluble under certain conditions, so they can be almost completely removed by creaming, centrifuging or washing, and this fact is utilized in the preparation of a special grade of purified rubber now marketed because of its greatly reduced tendency to

TABLE V

Substance added	Temperature (° C)	Period of heating (Hours)	$N_r$ Per cent	$N$ in crepes from creams diluted to 15 per cent (Per cent)
None .....	20	0	0.175	—
Caustic soda .....	50	1	0.179	—
Caustic soda .....	50	5	0.125	—
Caustic soda .....	50	24	0.079	—
Caustic soda .....	50	54	0.064	—
Caustic soda .....	50	76	0.038	—
Caustic soda .....	50	100	0.038	0.057
Caustic soda .....	50	173	0.029	—
Caustic soda .....	50	240	0.020	0.044
Caustic soda .....	70	18	0.018	0.033
Caustic soda .....	70	66	0.018	0.026
Caustic potash .....	70	24	0.044	—

absorb water. A study was therefore made of the influence of caustic soda and caustic potash on the distribution of nitrogen in latex.

Portions of commercial ammoniated latex treated with caustic soda solution so that they contained 2 per cent of alkali in the water phase and about 20 per cent of dry rubber were heated for periods of 1, 5, 24, 54, 76, 100, 173 and 240 hours at 50° C, and for 18 and 66 hours at 70° C. After each period of heating, the latex was creamed with sodium alginate solution, and the underlayer withdrawn and sampled after 24 hours.  $N_t$  and  $N_w$  determinations were made in the manner described, but to calculate  $N_r$ , it was necessary to apply a correction to  $N_w$ , which was too low, owing to the action of caustic soda on the underlayer during removal by drying of the ammonia of preservation, a small part of which would otherwise have contributed to the nitrogen content. The results given in Table V and Figure 1 show that, at 50° C, over one-half the nitrogenous material passed in one day from the rubber into the aqueous phase, but that subsequent removal was much slower, and also that the rate of removal at 70° C was about ten times that at 50° C.

A further experiment was made in which latex was treated with caustic soda in a similar manner, and heated at 70° C for one week. It was then creamed six times with sodium alginate, when it was estimated that the latex should contain



less than 1 per cent of the original serum substances if the caustic soda treatment had rendered them entirely soluble. A nitrogen determination on a clear dry film of purified latex gave 0.028 per cent, which indicated that about 4 per cent of the total nitrogen in the latex was still attached to the rubber in latex after one week's heating at 70° C. This residual nitrogen was not removed by acetone extraction.

A portion of the same latex was treated with caustic potash in a manner similar to that previously employed for caustic soda, and was heated at 70° C for

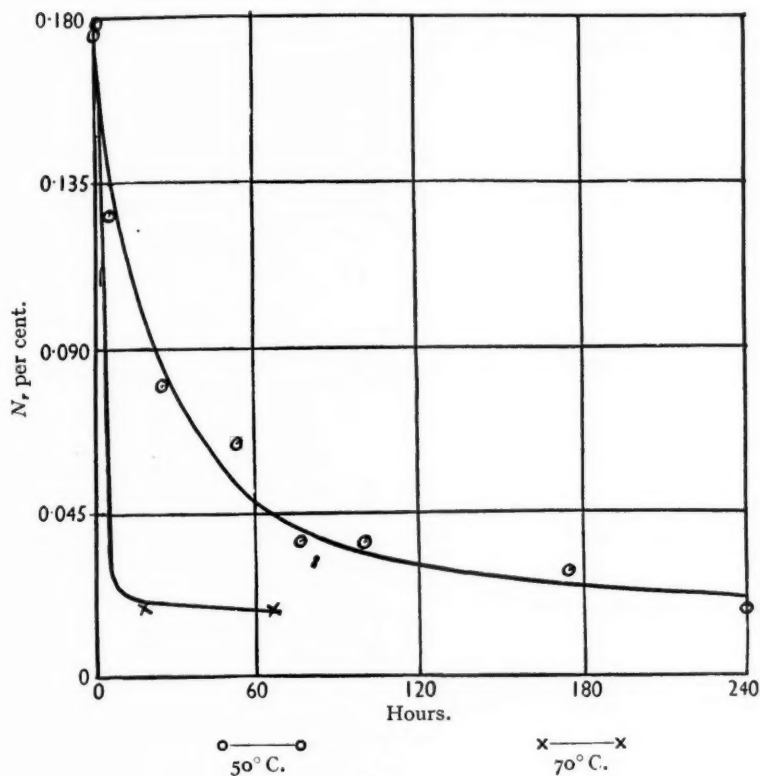


FIG. 1.

24 hours. The latex was considerably more stable and less viscous when cool than after a corresponding treatment with caustic soda, and  $N_r$  determination gave 0.044 per cent, indicating that the action of caustic potash is less rapid than that of caustic soda. The greater stability of caustic potash latex is, however, an advantage.

It is concluded that:

- (1) Treatment of latex with caustic soda removes almost all protein and other nitrogenous material from the rubber, whereas about 0.02 to 0.03 per cent of nitrogen (calculated on the rubber) is difficult to remove.
- (2) The rate of reaction is markedly affected by temperature, and to enable

the reaction to proceed in a reasonable time (less than one week) a temperature of over 50° C is required. At 70° C, one day is sufficient.

(3) Caustic potash is not so effective as the same concentration of caustic soda.

*Soaps.*—An alternative method for the removal of protein from the surface of the rubber particles in latex is to displace it by soaps which are known to replace proteins at an air-water interface<sup>3</sup>.

Experiments were made first with ammonia-latex treated with potassium oleate, so that the final mixture of latex, sodium alginate and soap contained 19.16 per cent of total solids and 1.39 per cent of soap. The distribution data obtained showed that  $N_r$  was reduced from 0.18 per cent to 0.035 per cent. Repeated creaming with a mixture of sodium alginate and soap in which 98 per cent of serum substances was removed gave a cream containing nitrogen equivalent to 0.034 per cent of the total solids, compared with 0.165 per cent for the control latex after a similar treatment with sodium alginate alone.

A similar experiment was carried out with the same latex, using 0.83 per cent of oleic acid in place of potassium oleate.  $N_r$  was found to be 0.080 per cent and, after purification by repeated creaming, the nitrogen in the total solids was 0.066 per cent. The purified cream was extremely stable, being only partly coagulated

TABLE VI

Potassium oleate in 100 g. of latex 19.1 per cent d.r.c. (Grams)	$N_w$ (Per cent)	$N_r$ (Per cent)	$N_t$ of purified latex (Per cent)
Nil	0.088	0.180	0.178
0.16	0.099	0.130	0.141
0.35	0.102	0.115	0.110
0.62	0.107	0.095	0.078
1.35	0.118	0.046	0.040
2.57	0.122	0.036	0.037

with 2 per cent acetic acid after dilution with an equal volume of water, and was still incompletely coagulated on boiling with excess of 10 per cent acetic acid.

The subject was studied further, using latex entirely preserved with sodium pentachlorophenate (0.9 per cent), to which potassium oleate was added in increasing proportions. An important advantage of this latex lay in the absence of ammonia; this made it unnecessary to evaporate the underlayer to dryness and to apply a correction to  $N_w$  on account of the action of potassium oleate on serum nitrogen during drying. A peculiarity of this latex was its tendency to separate rapidly into layers of different composition, causing difficulty in sampling and consequently in obtaining  $N_t$ . Once the feature was recognized, however, the necessary precautions were easily taken. Table VI shows the values for  $N_w$  and  $N_r$  for different amounts of added soap, and the last column contains the amounts of nitrogen present in the crepes obtained after repeated creaming to remove 98 per cent of the serum substances. The nitrogen contents of the purified crepes agree well with the calculated  $N_r$  values.

A further experiment was made in which the amount of added soap was increased to 5.66 per cent. Similar results were obtained,  $N_r$  remaining at 0.03 per cent in the presence of 3 per cent or more of soap. Thus the surface nitrogen was removed by the addition of 3 per cent of potassium oleate to the latex (19.1 per cent dry rubber content).

To determine the extent to which potassium oleate replace protein at the rubber-serum interface, the amounts of oleate present in the underlayer were

determined directly by taking advantage of the solubility of potassium oleate in 80:20 alcohol-water mixture, in which the bulk of the remaining serum components are insoluble. After acidification, the oleic acid which separated was extracted with ether, the ether solution was washed with distilled water till free of acid, and the oleic acid was determined after evaporation to dryness and solution in neutral alcohol by titration against decinormal caustic soda.

From the amounts of protein ( $N_r \times 6.25$ ) and potassium oleate on the rubber (calculated from the amount found by direct determination in the underlayer), it was possible to calculate directly the amount of soap replacing the protein which had passed into the serum. The results, set out in Table VII, show that the maximum replacement of protein occurred when 2 or more per cent of soap was dissolved in the aqueous phase. In conformity with the notation already adopted,  $S_w$  denotes the amount of potassium oleate in the underlayer (per cent water), and  $S_r$  the amount of potassium oleate in the rubber phase (per cent rubber).

If the action of soap is simply to replace protein at the rubber-serum interface, the weight of the residual rubber phase, *i.e.*, less soap and protein, should be

TABLE VII

Potassium oleate added to 50 g. of 40 per cent latex + 50 g. water and creaming agent (g.)	Total solids of mixture (g.)	Weight of rubber phase (g.)	Weight of potassium oleate found in serum (g.)	Weight of potassium oleate on rubber by difference (g.)	$N_r$ (Per cent)	Weight of rubber phase less protein and potassium oleate (g.)	( $S_w$ ) per cent of water	( $S_r$ ) per cent of rubber phase
Nil	21.27	19.08	Nil	Nil	0.180	18.87	Nil	Nil
1	22.27	19.19	0.71	0.29	0.082	18.80	0.92	1.54
2	23.27	19.39	1.30	0.70	0.045	18.63	1.68	3.61
3	24.27	19.62	1.98	1.02	0.029	18.56	2.52	5.21
4	25.27	19.72	2.82	1.18	0.034	18.50	3.58	5.98
5	26.27	19.74	3.75	1.25	0.029	18.45	4.79	6.34
6	27.27	19.60	4.95	1.05	0.033	18.51	6.31	5.37

constant throughout the series. However, all the latices treated with soap contained less residual rubber phase than did the control, and, further, when the difference of each from the control was plotted against  $S$ , a straight line was obtained, indicating that, in addition to protein, other substances are being replaced in constant ratio by potassium oleate at the rubber-serum interface (Figure 2).

The results suggest that the maximum concentration of soap at the rubber-serum interface is from 6 to 7 per cent of the rubber phase and is obtained by adding 5 per cent of soap to a latex containing about 20 per cent dry rubber. Addition of larger amounts of soap results in a higher concentration of soap in the serum and a smaller amount retained by the rubber. The action of soaps, such as potassium oleate, on the nitrogen distribution in latex may conveniently be summarized as follows:

- (1) Potassium oleate replaces protein and other serum components at present unidentified at the rubber-serum interface.
- (2) All except about 0.03 per cent (calculated on the rubber) of the nitrogen attached to the rubber is capable of removal by potassium oleate and, therefore, resides at the rubber-serum interface.
- (3) Maximum displacement of protein occurs when the aqueous phase contains about 2 per cent of potassium oleate and the concentration of soap at the

interface is about 5 per cent of the rubber phase and about 5 times the amount of displaced protein. For 20 per cent latex, this is equivalent to adding from 3 per cent of soap to the latex.

(4) Replacement of an unidentified substance continues up to a concentration of soap at the interface of nearly 7 per cent of the rubber phase, and is directly proportional to the amount of soap present at the interface. As the most surface-active substance would be last to be replaced by soap, these results indicate that the unknown substance is more surface-active than protein, and suggest that it may be the phospho-lipin sterol complex which is also thought to be associated with the rubber phase.

(5) The rubber surface appears to be saturated by about 7 per cent of soap calculated on the rubber, and addition of further soap results in a reduction of the amount associated with the rubber.

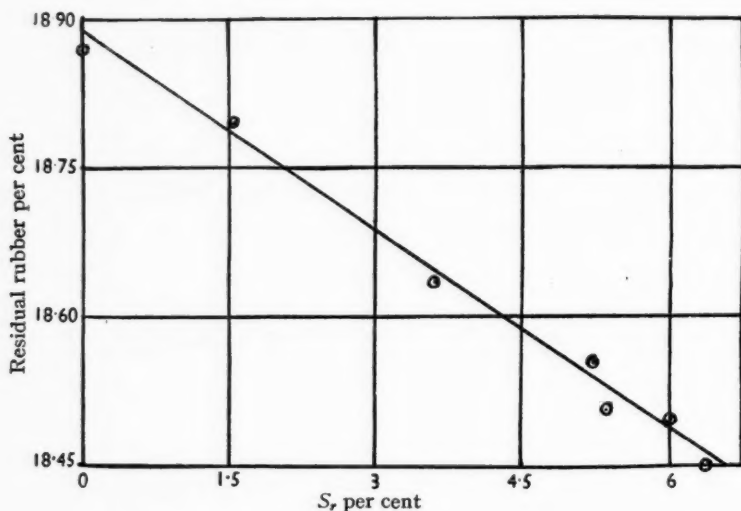


FIG. 2.

The main points of the investigation on the nitrogen distribution given in this paper may now be summarized briefly as follows:

(a) Approximately one-quarter of the total nitrogen of six months' old ammoniated field latex is attached to the rubber globules.

(b) Some nitrogen represented by an  $N$  of 0.02 to 0.03 per cent remains firmly attached to the rubber, and is not replaced by soaps or removed by caustic alkalis after heating at 70° C for one week. Therefore it is not surface nitrogen, and may be in chemical combination with rubber hydrocarbon.

(c) The remaining  $N_r$  represents chiefly surface protein which is partially desorbed at an alkaline pH by washing the latex, *e.g.*, dilution or repeated creaming; partly removed by proteolytic enzymes under the experimental conditions, which, however, may not have been the optimum; gradually but completely removed by strong alkalies; quickly and completely replaced by soaps such as potassium oleate.

(d) Evidence has been obtained for the existence of another substance more surface-active than protein at the surface of the rubber globules. This substance is replaced by soaps, and is possibly of a lipid nature.

*Distribution of acetone extracts and acid values.*—Ammoniated field-latex usually contains from about 12 to 14 per cent of non-rubber substances, of which approximately one-half are removed by extraction with water at room temperature of the partly dried film containing from about 7 to 10 per cent moisture, the remaining insoluble non-rubber substances being composed chiefly of protein and substances soluble in acetone or alcohol. For example, one batch of commercial ammoniated field-latex contained 14 per cent of non-rubber substances, composed of 8.5 per cent water-soluble material containing about one-half the latex nitrogen, whereas the extracted film contained about 2 per cent nitrogen, calculated as protein, and its degradation products, and 3.5 per cent of substances soluble in alcohol. In view of the high percentage of water-soluble non-rubber substances in latex, it is obviously essential to dry the latex thoroughly before extraction with acetone or alcohol to obtain reliable results. In laboratories, latex films are air-dried for 2 days at 30° C, followed by 4 days over calcium chloride at room temperature. The effect of incomplete drying is illustrated by the results obtained on commercial ammoniated field-latex. After 48 hours' air-drying, the acetone extract of the latex was 6.22 per cent, compared with 5.06 per cent after thorough drying. The acid values of the two extracts were, however, almost identical at 421 and 430 mg. potassium hydroxide per 100 grams of solids, respectively. Although the acetone and alcohol extracts of crepe or sheet rubber are almost identical, absolute alcohol extracts considerably more material than acetone from thoroughly dried latex, *e.g.*, 8.00 per cent for the latex just mentioned, including some further acids, the acid value rising to 502.

Acetone extract and acid value were among several properties of field latex from one source studied by Rhodes<sup>4</sup> over a period of 14 months. The acetone extract of films from fresh field latex varied from 3.2 to 3.8 per cent, and its acid value from 120 to 180. Ammoniation brought about a decrease in both values, which increased, however, on storage for 50 days to more than the value for fresh latex, the increase in acid value being the more marked. The final range of acetone extracts was from about 3.7 to 4.1 per cent, and of acid values from about 260 to 380. The results now presented show that this increase continues up to 18 months' storage, when dry films from old ammoniated latex may give acetone extracts of over 5 per cent, and acid values of over 500.

The acid value of the acetone or alcohol extract of dried latex was found to include large amounts of water-soluble acids, long chain fat acids comprising from one-third to one-half the total acid value. The extract also contained about 10 per cent of the total latex-nitrogen. These observations recall the maturation of rubber, a process of preparation which greatly favors bacterial and enzymatic activity causing the hydrolysis of proteins and sugars, and indicate that similar changes occur in ammoniated latex. Matured rubber gives an acetone extract containing a high proportion of water-soluble acids, which Bruni and Levi<sup>5</sup> identified as  $\alpha$ -aminovaleric,  $\alpha$ -aminocaproic (norleucine) and phenylacetic acids, together with tetramethylenediamine and pentamethylenediamine, from degradation of proteins. Maturation also causes a rapid and marked reduction in nitrogen content of the resulting rubber, *i.e.*, by chemical decomposition of proteins to form water-soluble products.

Data for the distribution of acetone-extractable material between rubber- and water-phases in latex are given in Table VIII. (A.E.)<sub>w</sub>, (A.E.)<sub>r</sub>, and (A.V.)<sub>w</sub>,

(A.V.)<sub>r</sub> relate to the distributions of acetone extract and its acid value, and are defined in a similar manner to  $N_s$ ,  $N_r$ , and  $S_s$ ,  $S_r$ .

The results show that ammoniated latices are just as variable with respect to acetone-soluble non-rubber substances as of nitrogenous substances. Experiments on the second series of latices prepared from the same parent latex already given in Table III showed that (A.E.)<sub>r</sub> for this series is substantially independent of particle size, but that (A.V.)<sub>r</sub> shows definite signs of being largely a surface property (Table IX), as it is the same for the two samples containing particles which on the whole are of average diameter, is low for centrifuged latex containing large particles, and is high for the two skim-latices containing small particles.

TABLE VIII

field-latex Ammoniated	(A.E.) <sub>w</sub> (Per cent)	(A.E.) <sub>r</sub> (Per cent)	(A.V.) <sub>w</sub> (Per cent)	(A.V.) <sub>r</sub> (Per cent)
C .....	0.61	3.22	63	208
D .....	0.85	2.38	101	189
E .....	0.82	3.75	121	295

TABLE IX

Description of latex	Original d.r.c. (Per cent)	(A.E.) <sub>w</sub> (Per cent)	(A.E.) <sub>r</sub> (Per cent)	(A.V.) <sub>w</sub> (Per cent)	(A.V.) <sub>r</sub> (Per cent)
Parent latex (C) .....	38.0	0.61	3.22	63	208
Centrifuged cream .....	62.6	0.17	2.99	33	105
Centrifugal skim .....	26.0	1.46	3.08	161	287
Centrifugal skim creamed..	53.9	0.63	2.90	59	207
Parent latex creamed.....	57.7	0.21	3.09	28	207

TABLE X

Dry rubber content (Per cent)	(A.E.) <sub>w</sub> (Per cent)	(A.E.) <sub>r</sub> (Per cent)	(A.V.) <sub>w</sub> (Per cent)	(A.V.) <sub>r</sub> (Per cent)	(A.E.—Soap) <sub>r</sub> (Per cent)
2.5	0.07	1.94	7.1	80	1.52
5	0.16	2.11	12.0	113	1.52
10	0.33	2.17	22.7	139	1.44
20	0.73	2.32	49.7	143	1.57

The effect of dilution of latex on the distribution of the acetone extract and its acid value was studied by creaming from latices of 2.5, 5, 10, 20 per cent dry rubber content, respectively. The results, given in Table X, indicate that ammonium soaps are removed from the surface of the rubber particle on dilution, and that the residual portion of the acetone extract is unaffected.

The results obtained in this section may be summarized as follows:

(1) To obtain reliable figures for the amounts of substances soluble in acetone or alcohol in films from preserved latex, it is necessary to subject the film to thorough drying.

(2) The acetone extract may be over 5 per cent, and its acid value exceed 500 when latex is old (18 months).

(3) Absolute alcohol extracts considerably more material than acetone from dry films from preserved latex, and the extract may also include more substances of acidic character.

(4) The acid value of the dry film includes large amounts of water-soluble acids. Long-chain fat acids comprise only from about one-third to one-half the



total acid value. The extract also contains appreciable amounts of nitrogen, which, by analogy with matured rubber, is probably present as amino acids and amines from degradation of proteins.

(5) Distribution data show that  $(A.E.)_r$  and  $(A.V.)_r$  vary considerably among latices, and that the part of  $(A.E.)_r$  represented by  $(A.V.)_r$  is largely a surface property. There are indications that the remainder of  $(A.E.)_r$  is largely contained within the rubber globule, but the evidence is inconclusive, and further work on the acetone and alcohol extracts of dried films is required before complete details of the distribution of these materials in preserved latex can be obtained.

*Changes in properties of latices on storage.*—These experiments were carried out on four experimental latices prepared by the Rubber Research Scheme, Ceylon. They included two field-latices ammoniated to 0.5 and 0.8 per cent, respectively, and two creamed concentrates ammoniated to 0.4 and 0.5 per cent, respectively, the first three of which were from the same parent latex and the

TABLE XI

Latex	Date of examination	D.R.C. (Per cent)	Ammonia (Per cent)	Stability (Rev.)	Distribution of nitrogen		Distribution of acetone extract		Distribution of acid value of the acetone extract	
					$(N_w)$ (Per cent)	$(N_r)$ (Per cent)	$(A.E.)_w$ (Per cent)	$(A.E.)_r$ (Per cent)	$(A.V.)_w$ (Per cent)	$(A.V.)_r$ (Per cent)
A	Jan. 1938	39.24	0.48	39,200	0.181	0.179	0.70	2.94	82.5	185
	Jan. 1939	39.17	0.49	26,000	0.198	0.135	0.54	3.28	46.0	266
B	Jan. 1938	39.86	0.80	45,000	0.183	0.144	0.53	2.93	51.7	176
	Jan. 1939	39.79	0.80	25,000	0.194	0.108	0.87	2.38	40.7	220
C	Jan. 1938	52.84	0.41	21,000	0.120	0.133	0.54	2.79	62.6	163
	Jan. 1939	52.78	0.42	23,000	0.102	0.136	0.32	2.94	61.6	166
D	Jan. 1938	57.44	0.49	18,000	0.100	0.131	0.54	2.43	57.0	149
	Jan. 1939	57.23	0.52	16,000	0.094	0.139	0.44	2.50	78.3	122

fourth harvested a few weeks later from the same source. The samples were tested before and after twelve months' storage in glass in the dark for dry rubber content, ammonia content, distributions of nitrogen, acetone extract and its acid value, and also for resistance to coagulation by stirring in the presence of zinc oxide, according to the method described by Davey and Coker<sup>6</sup>. The results of the two sets of tests are given in Table XI. They show that there was little change in either the dry rubber or ammonia contents of all four latices, but that a complicated series of changes occurred in the other properties studied, which was greater in the latices containing 38 to 40 per cent of rubber and less marked in the creamed latices. The samples A and B containing 38 to 40 per cent of rubber showed a decrease in stability towards stirring in the presence of zinc oxide and a decrease in  $N_r$  values, whereas the creamed latices C and D altered little both in stability and in  $N_r$  during the year. Large changes occurred in the distribution of acetone extract and its acid value in the two 38 to 40 per cent latices, and relatively small changes in the two creamed latices, *e.g.*,  $(A.V.)_r$  in A and B showed marked increases.

These results, together with those described in the previous section, are explained on the basis of the existence in fresh latex of complexes from which proteins and fat acids are derived. The existence in fresh latex of chemical com-

plexes whose components are liberated on hydrolysis has been indicated by the work of Roberts<sup>7</sup>. In fresh latex the hydrolyzing agents are the naturally occurring enzymes and bacteria. Ammoniation of the latex checks bacterial activity, which no doubt accounts for the diminution in acetone extract and acid value of films from freshly-ammoniated fresh latex recorded by Rhodes<sup>4</sup>, and, if sufficient ammonia is present, bacterial action is completely inhibited; for instance, in 7 days for latex containing 0.7 per cent ammonia<sup>8</sup>. Subsequent changes in the chemical composition of ammoniated latex are due to the joint action of enzymes and ammonia tending (1) to liberate and degrade proteins, causing those in the adsorbed layer round the globules in part to pass into the aqueous phase (decrease in  $N_r$ ), and (2) to liberate fat acids which accumulate as ammonium soaps at the rubber-water interface (increase in  $(A.V.)_r$ ). Process (1) tends to decrease, process (2) to increase the resistance of the latex towards coagulation by acids. Evidence of the existence of opposing tendencies affecting the resistance of the latex towards coagulation is also given by Rhodes's experiments<sup>4</sup>, which indicated a small but highly significant positive correlation between the resistance to coagulation of latex against stirring in the presence of zinc oxide and acid value after 10 days' storage, and a small but highly significant negative correlation after 50 days' storage. The displacement of protein by soaps at the interface apparently occurs mostly during the first 50 days after ammoniation, as  $(A.V.)_r$  after 18 months is no higher than the acid value of crepe rubber. The decrease in stability towards electrolytes on storage of commercial ammoniated field-latex seems to be due chiefly to the reduction in surface nitrogen, as the increase in  $(A.V.)_r$  is not sufficient to compensate for the loss of surface proteins.

*Structure of the rubber globule in preserved latex.*—(1) *The interior.*—The experiments already described indicate that within the rubber globule there is approximately 0.02 per cent nitrogen and some material soluble in alcohol or acetone. No evidence has so far been obtained which gives a clue to the nature of the end-groups in the long-chain molecules of rubber, but it is of interest that the above amount of nitrogen on the basis of two nitrogen atoms per molecule would indicate a mean molecular weight of 140,000.

(2) *The boundary.*—At the boundary of the rubber globule is concentrated protein, soaps and other surface-active substances, probably of lipid nature. The exact arrangement of these substances at the surface is not known but, from analogy with their alignment at the water-air interface<sup>9</sup>, it may be suggested that they exist as a complex film, which, at sufficiently great compressions, may become a duplex layer with the hydrophobic lipid portion next to the rubber phase and the hydrophilic proteins and soaps on the outside. It is considered that the duplex layer is unlikely to be more than about 40 Å.U. thick, assuming that the lipid portion is thinner than a fat acid monolayer, which is known to be about 25 Å.U. thick, and that the thickness of a compressed film of latex protein is about 15 Å.U.<sup>10</sup> The ratio of soap to protein in the outer hydrophilic layer is probably of considerable technical importance in view of the observations of Kemp and Twiss<sup>11</sup> that the isoelectric point of an aqueous dispersion of the acetone extract from crepe rubber is at a pH value of  $2.1 \pm 0.1$ , although it should be remembered that the experimental conditions were probably not those existing when soap is orientated at the rubber-water interface.

*Acknowledgments.*—The author is indebted to the London Advisory Committee for Rubber Research (Ceylon and Malaya) for permission to publish the results of this investigation, to his colleagues, G. Martin and W. G. Wren, for much helpful discussion and advice, and to M. W. Philpott, Chemist to the Rubber Research Scheme, Ceylon, for the preparation of many of the samples.

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# POSITIVELY CHARGED LATEX \*

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Latex, like many other colloidal systems, owes its stability to a large extent to the electrical charge carried by each particle in suspension. One possible explanation<sup>2</sup> of how the particles become charged is that the protein adsorbed on the rubber hydrocarbon is capable of ionizing to a slight extent, both as an acid and as a base, much in the same manner as do amino acids. In a highly basic solution the rubber particle acquires a negative charge; whereas in an acid solution the charge is positive. At some stage between strongly acid and strongly basic solutions, the ionization of the adsorbed protein layer would be as much acidic as basic, and the particle would have no net charge. This is known as the isoelectric point, and has been found to be at a pH of 4.2<sup>3</sup>. At or near the isoelectric point, the latex is very unstable, and coagulates rapidly. The charge carried by the particle may, of course, be due also to adsorption of ions from solution.

The latex particles are normally negatively charged, but the sign of the charge can be reversed by the addition of acid<sup>4</sup>, by the presence of polyvalent cations<sup>5</sup>, and more recently it has been shown that cationic soaps<sup>6</sup> may reverse the charge. In a cationic soap the positive ion is a long chain, and the negative ion is a halide, sulfate, etc. The hydrophilic group attached to the long chain of carbon atoms is a quaternary ammonium, sulfonium, or phosphonium group.

The authors felt that, because positively charged latex seems to have some commercial possibilities, it would be of interest to attempt to prepare latex suspensions of reversed charge of higher concentrations than those used by Blow<sup>6</sup>, which were apparently around 5 per cent.

The latex used was a centrifugally concentrated type containing 63 per cent total solids and 0.55 per cent ammonia. Of the cationic soaps studied the following seemed to show the most promise (these were of commercial grade):

Cetyl pyridinium bromide (which we shall refer to as).....	A
Cetyl trimethylammonium bromide (which we shall refer to as).....	B
Diethylaminoethylstearyl amidoacetate (which we shall refer to as).....	C

By trial it was found that about 5 per cent on the dry rubber content of the latex was a satisfactory amount of cationic soap to use. Less than this amount did not satisfactorily reverse the charge; more had no additional beneficial effect.

The charge of the particles was determined by using platinum electrodes attached to a source of direct current, and noting the direction of migration with an ultramicroscope, or observing on which electrode the rubber deposited.

A standard procedure was adopted to determine the relative values of these soaps for the latex used. One hundred and twenty grams of 63 per cent latex were diluted with 310 grams of water. This diluted latex was poured into 80 grams of 5 per cent cationic soap solution. Sixty cubic centimeters of the resulting solution were then taken as a standard amount. Varying quantities of 5 per cent acetic acid were added to the standard solutions, and the pH of each was determined with a glass electrode. After 24 hours the samples were examined, and the

\* Reprinted from the *India Rubber World*, Vol. 104, No. 1, pages 39, 50, April 1, 1941.

pH range in which the solution did not cream was noted. The results are as shown in the following table.

Soap A.....pH of a 5 per cent solution = 1.8		
cc. of acid added (5 per cent)	pH	Remarks
0	9.7	Creamed-paste on top
2	9.0	Creamed-paste on top
2.75	7.8	Creamed-paste on top
3	6.6	Slight creaming fluid on top
3.75	6.13	Very slight creaming-fluid on top
4	6.0	Very slight creaming-fluid on top
4.25	5.8	No creaming
5	5.2	No creaming
7	4.7	No creaming
10	4.4	No creaming
Soap B.....pH of a 2 per cent solution = 3.1		
0	9.7	Creamed-paste on top
1	9.5	Creamed-paste on top
2	8.9	Creamed-paste on top
3	7.7	Creamed-paste on top
4	5.7	Creamed-fluid on top
5	4.7	No creaming
10	4.4	No creaming
Soap C.....pH of a 5 per cent solution = 2.5		
0	9.8	Creamed-paste on top
3	7.8	Creamed-paste on top
4	5.8	Creamed-paste on top
5	5.2	Creamed-paste on top
6	4.9	Creamed-fluid on top
7	4.8	Creamed-fluid on top
10	4.6	Creamed-fluid on top

Soap B was used as a 2 per cent solution because, at a concentration of 5 per cent, it was too viscous to handle easily. This dilution was compensated for in preparing the standard samples.

The terms "paste on top" and "fluid on top" in the table are merely relative. They serve as a crude method of describing the nature of the top layer which results when creaming occurs. Since the technique of preparing the samples was found to have an important effect on the results, no effort was made to establish more closely the pH at which creaming occurred. It was felt that there was no justification for attempting more accurate values, since change in the kind of latex, method of mixing, or concentration of reagents would affect the values to a greater extent than the limits already determined.

From the table it can be seen that for Soap A a pH of six is the limit, and for B the limit is at a pH of five. With Soap C the latex creamed at all values of pH tried.

To some solutions which had creamed during the 24-hour period, acetic acid was added to bring the pH down to values at which freshly prepared solutions were stable. In many cases it was found that the solutions did not cream again.

It was found that addition of a fairly concentrated latex (about 30 per cent dry rubber, or greater) to Soap A, utilizing about 5 per cent soap on the rubber, caused gelation that resulted in a pasty mass resembling soft putty. Addition of enough acid to lower the pH below six caused the mass to become as fluid as ordinary latex, with no tendency to cream. This change was due to a change in pH, since addition of water did not produce a stable solution. The concentration of rubber was gradually increased until stable suspensions of 30 per cent dry rubber content were obtained. It is felt that, with more efficient stirring, stable positively charged latex solutions of still higher rubber content can be prepared.

The effect of the addition of such compounds as dioctyl sodium sulfosuccinate, isopropylnaphthalene sodium sulfonate, and the tauric acid ester of the sodium salt of isethionic acid on latex, before and after the addition of cationic soap, was investigated. The materials tend to stabilize negatively charged latex, and the first two compounds listed above prevented cetyl pyridinium bromide from reversing the charge, when the amount of cationic soap was 5 per cent on the dry rubber content. It was found that a stable positively charged latex could be prepared, in the presence of the third compound listed above, with cetyl pyridinium bromide and acetic acid. The dry rubber content of such a preparation had a maximum value of about 20 per cent.

The authors wish to express their thanks to E. I. du Pont de Nemours & Co., Inc., for supplying cetyl pyridinium bromide and cetyl trimethylammonium bromide for use in this investigation.

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# ORGANIC ANALYSIS OF HEVEA LATEX. IV<sup>1</sup>

## AMINO ACIDS \*

R. F. A. ALTMAN

### I. INTRODUCTION

The presence of amino acids in fresh latex was reported by Belgrave<sup>2</sup> in 1925. On the basis of certain considerations, he considered it improbable that his experiments involved any profound changes in the original state of the nitrogen compounds. Accordingly the amino acids which he isolated must have been present in the free state in latex. It may be noted here that Belgrave's experiments did not completely exclude either chemical or enzymatic hydrolysis of proteins. Indeed, his amino acids were separated from a serum which was prepared by acidifying fresh latex with acetic acid (20 cc. of 10 per cent acid per liter of latex) and heating gently, with no precautions whatever for inactivating any proteolytic enzymes which may have been present.

Aside from Belgrave's paper, there have been only two published references to the presence of amino acids in rubber or latex. Whereas Whitby, Dolid, and Yorston<sup>3</sup> reported the isolation of valine from the acetone extract of crepe rubber, McGavack and Rumbold<sup>4</sup> were able to isolate d-alanine from the serum of old ammoniated latex. There is no reason whatever for assuming from these observations that valine and alanine also occur free in latex. Indeed it would be impossible to give any guaranty that there was no hydrolytic degradation of proteins in the sample.

In view of this situation it seemed highly desirable, as part of a systematic organic analysis of latex, to investigate more exactly the free amino acids which are present in latex. In addition to Belgrave's observation a preliminary analysis of fresh bottom latex which had been prepared for other purposes<sup>5</sup> indicated that free amino acids actually do occur in latex. The object of the present paper is to identify the amino acids occurring in latex and, so far as is feasible, to determine the quantity also.

### II. METHOD FOR SEPARATING FREE AMINO ACIDS FROM FRESH LATEX<sup>6</sup>

The method described below for separating amino acids from latex is based on preventing chemical or enzymatic hydrolysis of proteins as completely as possible.

A liter of latex was allowed to flow in a thin stream, while agitating with a high speed mechanical stirrer, into 9 times its volume of absolute alcohol which contained a little toluene and was preheated to about 60° C. The spongy rubber coagulum which formed regularly was lifted out of the alcohol with tweezers and laid on a Büchner funnel, which served as a strainer. By creping the coagulum very thin without washing it, the alcoholic solution of proteins precipitated within it was drawn off. The crepe, which was rolled between filter papers, was then heated 3 hours to gentle boiling with half of the clear alcohol solution under a reflux condenser. The alcoholic extract thus obtained, which was distinctly yellow, was drained off from the roll of rubber and was concentrated by vacuum distil-

\* Translated by Julian F. Smith for RUBBER CHEMISTRY AND TECHNOLOGY from Mededeeling No. 26 van de Afdeling Rubber Research van het Proefstation West Java, Buitenzorg, Java. Also published in *Archief voor de Rubbercultuur* Vol. 24, No. 8, pages 647-654, August 1940.

lation. Meanwhile the roll of rubber was again boiled 3 hours with the other half of the clear alcohol solution, and this second alcoholic extract too was evaporated in a vacuum. The distillation residues formed a turbid faintly acid, yellow liquid in which lecithins<sup>7</sup> were clearly recognizable as a buttery substance. The total volume was about 500 cc. After adding a like volume of hot water there were first added, with vigorous stirring, 60-75 cc. of 5 per cent tannin solution, then 30-35 cc. of 25 per cent acetate solution, drop by drop. Proteins, phosphatides, plant acids, etc. are practically completely precipitated by this treatment (it appears, as set forth below, that amines are not completely precipitated). Use of too much lead acetate must be avoided, since this would also precipitate some of the amino acids (tyrosine and asparagic acid).

The thick yellow precipitate settles rapidly and after standing 30 minutes most of the solution can be decanted as a clear liquid. By stirring for a time with a fresh quantity of water, allowing the precipitate to settle and decanting the solution the precipitate can be thoroughly washed. Finally it is sucked dry on a Büchner funnel. When hydrogen sulfide is passed into the combined clear solutions, the lead sulfide is filtered off, and the liquid is evaporated in a vacuum, a pale brown syrup is obtained, amounting to about 18.5 grams after drying for a week in a vacuum-desiccator (after 3 days in the desiccator, beautiful crystals, identified as quebrachitol, began to separate from the thick syrup).

In order to separate amino acids from the mixture thus obtained, 10 per cent sodium carbonate and 25 per cent mercuric acetate solutions are added alternately to the 20 per cent aqueous solution as described by Neuberg, until there is no longer any formation of a white precipitate. To precipitate mercury carbamates as completely as possible the reaction mixture is diluted with eight times its volume of alcohol. The precipitate is allowed to settle, the clear solution (excellent analytical material for a study of sugar and quebrachitol derivatives occurring in latex, which is to be taken up later) is decanted, the precipitate is filtered with suction as thoroughly as possible, and washed first with 80 per cent and then with 50 per cent alcohol until the filtrate is no longer alkaline. The wet precipitate is then suspended in water and mercury compounds are decomposed by hydrogen sulfide. After filtering off the mercuric sulfide with suction the clear filtrate is evaporated in a vacuum desiccator. The yield of this mixture of amino acids, contaminated with other substances (nitrogen bases), is 1.45 to 1.50 grams. It may be noted that precipitation of amino acids by Hg acetate from a solution made alkaline with sodium carbonate is not strictly quantitative but is about 95 per cent complete.

### III. ANALYSIS OF THE AMINO ACID MIXTURE

Before actual analysis of the isolated acids, the aqueous solution of the mixture described in the preceding paragraph is acidified with sulfuric acid (the solution must contain about 5 per cent sulfuric acid), so that any amines (see below) which may be present can be completely precipitated with 10 per cent phosphotungstic acid, which is added until it no longer forms a precipitate within 10 seconds<sup>8</sup>. It was found that the resulting dark brown precipitate contains no amino acids but does contain amine bases (the weight of amine hydrochlorides obtained in this way is 0.11 to 0.12 gram per liter of initial latex), *i.e.*, amines and betaines<sup>9</sup>.

The filtrate from the phosphotungstate precipitate is freed from excess phosphotungstic acid by shaking with finely divided barium hydroxide, and the excess of the latter is removed by hydrogen sulfide<sup>8</sup>. Suction filtration yields a practically

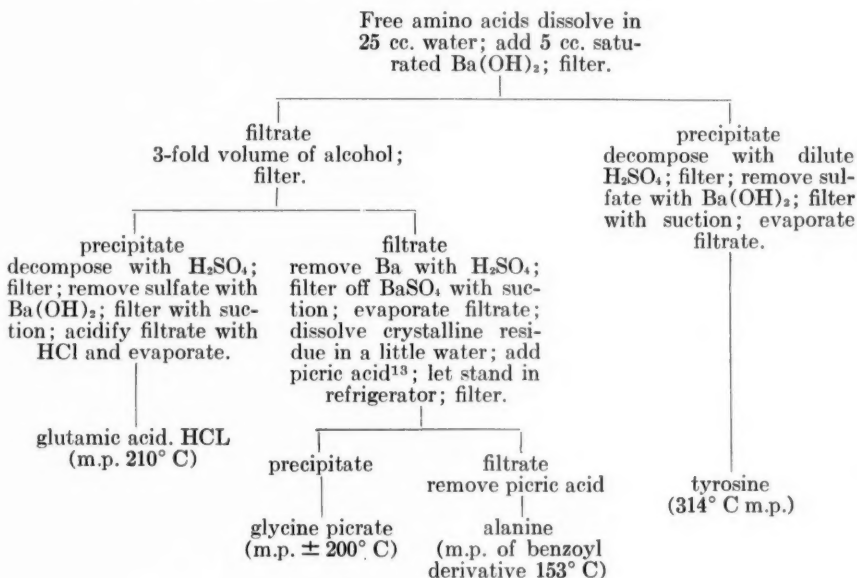
water white solution from which about 0.80 gram of dry residue can be obtained by evaporating in a vacuum.

This mixture of purified amino acids was analyzed by the Brazier method<sup>11</sup>, as modified by Altman<sup>10</sup>. It may be recalled that the method is based on differences in solubility of the copper salts of the amino acids in MeOH and in water. Before forming the copper salts, certain amino acids are separated from the mixture as a "prefraction" by a suitable method (see Parts I and II). Readers being referred to the original publications, all that is necessary is a brief summary of results, clarified where necessary by additions to the previous analytical outline.

Thus it may be noted that the small quantities of proline and tyrosine make it unnecessary to separate the prefraction. Accordingly the amino acids (800 mg.) are directly converted to their copper salts by boiling with cupric carbonate. The salts are then separated into main fractions (a), (b) and (c) (see below). Attention is directed to the separation of isoleucine, tyrosine, glycine and cystine, which are either absent from Brazier's outline or are now separated in a different place (tyrosine).

a) *Copper salts: soluble in absolute methanol*.—The amino acid mixture (150 mg.), freed from copper and evaporated to dryness, is first digested with cold absolute ethanol, which dissolves only proline (identified as the cadmium chloride salt; p. 155°). Valine and isoleucine are readily isolated from the insoluble portion, as described by Levene and Van Slyke<sup>12</sup>. To the aqueous solution (1:7) there is first added 0.5 cc. of 25 per cent ammonium hydroxide, then (dropwise while shaking) 0.5-0.6 cc. of 25 per cent lead acetate, which precipitates isoleucine as  $Pb(C_6H_{12}O_2N)_2$ , while valine remains in solution. The precipitate is filtered off, and both acids (precipitate and filtrate) are regenerated by adding hydrogen sulfide, filtering off lead sulfide, and evaporating the solution; m.p. of valine 305° C; m.p. of isoleucine 285° C.

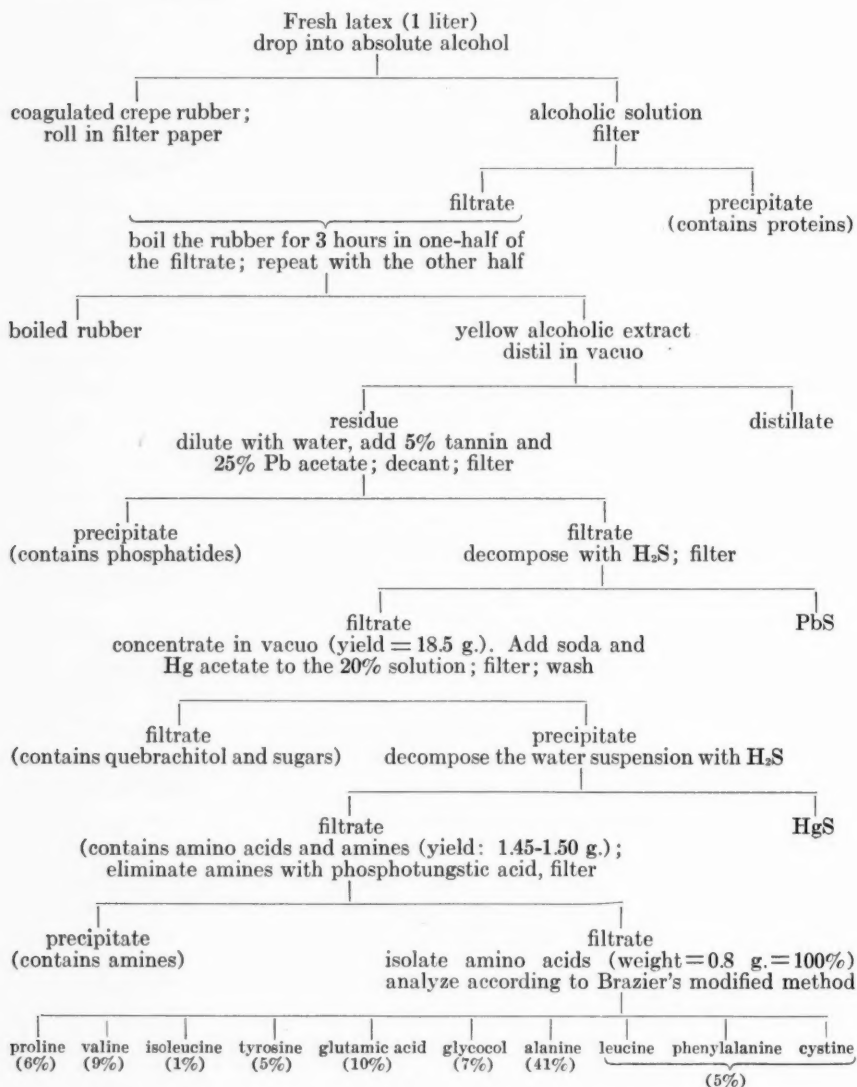
b) *Copper salts: methanol-insoluble, water-soluble*.—Amino acids in this fraction (dry weight about 600 mg.) were analyzed as follows:



c) *Copper salts: methanol-insoluble, water-insoluble.*—The amino acids liberated therefrom have a dry weight of about 40 mg. In addition to leucine (identified by conversion to leucinuric (?) acid, m.p.  $\pm 200^{\circ}\text{C}$ ) phenylalanine and cystine were qualitatively identified in the mixture, the former as described by Kapeller-Adler<sup>14</sup>, the latter as described by Fleming<sup>15</sup>.

#### IV. SUMMARY

The following scheme is a summary of the investigations.



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# ORGANIC ANALYSIS OF HEVEA LATEX. V

## AMMONIA, AMINES AND BETAINES \*

R. F. A. ALTMAN

### I. INTRODUCTION

The presence of ammonia in serum or latex has been reported by Gorter<sup>1</sup> and by Bishop<sup>2</sup>. The latter obtained approximately 6 mg. of ammonia (5 mg. of nitrogen) by steam-distilling 100 cc. of fresh latex containing 1 per cent of magnesium oxide. It may be noted that innumerable nitrogen compounds (amines, amides, amino acids, etc.) are unstable in alkaline medium, especially when heated to 100° C, and may give off ammonia or other volatile bases. Gorter's experiment was purely qualitative, and was concerned with serum obtained by coagulation with acetic acid.

In a previous paper<sup>3</sup> the present author called attention to the presence of amines and betaines in fresh latex. So far as could be ascertained, there had been nothing on this subject in the literature. The investigation of Klein and Steiner<sup>4</sup> shows amines to be phytochemically important compounds and, in all probability, these substances and betaines have practical importance in rubber chemistry as well, since they may belong to the much-discussed but as yet unidentified "natural age-resisters" in rubber. (It may be recalled that various vulcanization accelerators and antioxidants in current use are amines.) We hope to return to this subject later.

### II. SEPARATION OF NITROGENOUS BASES FROM FRESH LATEX

An alcoholic extract is prepared in the same manner as has been described for preparing amino acids from latex<sup>3</sup>; this is evaporated in a vacuum in an atmosphere of carbon dioxide, diluted with water, treated with 25 per cent lead acetate solution (add no tannin) until further addition barely ceases to form a precipitate. By filtering off the precipitate with suction, a clear filtrate is obtained, which can be freed from lead by hydrogen sulfide. The resulting solution is distinctly acidified by a little dilute sulfuric acid if necessary, and distilled in a vacuum to a volume of 400 cc. To the residue are added successively about 20 grams of strong sulfuric acid (the solution must contain 5 per cent sulfuric acid) and sufficient 10 per cent phosphotungstic acid solution (about 125 cc.) to cease forming any precipitate within 10 seconds after being added.<sup>5</sup> Any ammonia, amines or betaines present in the reaction mixture are practically quantitatively precipitated by this treatment. After standing 24 hours, the precipitate is filtered off with suction, washed with 5 per cent sulfuric acid and suspended in dilute alcohol or aqueous acetone<sup>6</sup>. Ice in lumps is added plentifully to this suspension, and then an excess of finely divided barium hydroxide. After shaking vigorously for one hour, the precipitate is filtered off with suction and washed with water. To avoid any loss of volatile bases, excess dilute sulfuric acid is added to the suction flask before filtering. The acid reaction of the filtrate, which is contaminated with

\* Translated by Julian F. Smith for RUBBER CHEMISTRY AND TECHNOLOGY from Mededeeling No. 27 van de Afdeling Rubber Research van het Proefstation West Java, Buitenzorg, Java. Also published in *Archief voor de Rubbercultuur*, Vol. 25, No. 1, pages 1-13, January 1941.



barium sulfate, is reduced with barium hydroxide, after which 50 cc. of normal hydrochloric acid is added, and the mixture is now for the first time entirely freed from sulfuric acid by barium hydroxide. After filtering off the barium sulfate and evaporating to dryness in a vacuum, the filtrate yields on the average 0.65 gram of a brown mainly crystalline substance per liter of original latex. This substance contains the hydrochlorides of nitrogenous bases present in latex.

In following the procedure just described, allowance must be made for the possibility that the phosphatides present in boiling alcohol<sup>3</sup> may be decomposed into their component parts<sup>7</sup>. This may give rise to choline, a base which in its turn may be decomposed, with formation of trimethylamine; in fact we found that volatile bases are liberated when rubber is extracted with boiling alcohol. By fitting the reflux condenser used in this extraction with a Peligot flask containing dilute hydrochloric acid, so that it is sealed airtight, it is possible to obtain a nearly negligible amount (never more than 3 mg. per liter of latex after boiling 6 hours) of a crystalline hydrochloride which can be identified microchemically<sup>4</sup> as trimethylamine hydrochloride,  $\text{Me}_3\text{N} \cdot \text{HCl}$ . The amount of choline is also small, since it was never possible to isolate more than 9 mg. per liter of latex. Although it may be true that the above-mentioned saponification of phosphatides does take place, it should not have any perceptible influence on the results.

### III. METHOD OF ANALYZING THE MIXED HYDROCHLORIDES

After various preliminary experiments, a method was developed which gives very satisfactory separation of the components of the mixture described in the preceding paragraph. No complete separation is possible in this case, and the percentages stated below cannot do more than express the approximate yields of the various fractions (averages of three determinations).

The sample (cf. the analysis chart below; 650 mg.=100%) is repeatedly extracted with boiling 96 per cent ethyl alcohol, which dissolves most of the material. The insoluble residue ( $a=19\%$ ) is set aside, while the solution, the volume of which is kept as small as possible (20-25 cc.) is treated with 5 cc. of saturated alcoholic mercuric chloride solution. This precipitates various betaines (glycine-betaine, trigonelline, choline), while the amines and other betaines (stachydrine, etc.) remain in solution<sup>8</sup>. The initially amorphous white precipitate is allowed to stand 48 hours in a refrigerator, at the end of which time all but a small proportion is crystalline. By filtering with suction, washing with cold water, and repeatedly digesting the noncrystalline component, a complete separation can be achieved by the precipitate (c) and solution (b).

The precipitate is very finely suspended in water and freed from mercury by passing in hydrogen sulfide. After filtering off the hydrogen sulfide with suction and evaporating to dryness in a vacuum, a residue is left ( $c=42\%$ ) which consists chiefly of colorless flat rectangular platelets. When recrystallized from the least possible quantity of 90 per cent alcohol, these crystals yield a proportionately large quantity (32 per cent) of beautiful lustrous flat platelets which melt at  $260^\circ\text{C}$ , and were identified as trigonelline hydrochloride (fraction  $c_1$ ). When the mother liquor is evaporated to dryness and the residue is extracted with a little 96 per cent ethyl alcohol, the uncrystallized remainder of the trigonelline hydrochloride (3 per cent) remains as an insoluble residue. The portion which is soluble in 96 per cent ethyl alcohol leaves on evaporation a residue, which is extracted in the completely dry state with a small amount of hot absolute ethyl alcohol. A small portion remains undissolved (fraction  $c_2=2\%$ ); the soluble component

leaves on evaporation a partially crystalline residue (needles and hexagonal platelets) and partly syrupy hygroscopic residue (fraction  $c_3=4\%$ ).

The alcoholic solution *b* containing mercuric chloride is cautiously evaporated to dryness; the residue is taken up in water and freed from mercury by hydrogen sulfide. After evaporating the solution to dryness a substance ( $b=35\%$ ) is obtained in which all kinds of crystal formations can be observed. The fact that this fraction contains no substances soluble in boiling chloroform indicates the absence of dimethylamine, trimethylamine, isobutylamine and isoamylamine.

Fraction *b* is analyzed at the same time as the first fraction *a*. For this purpose, the combined aqueous solutions are made alkaline with saturated barium hydroxide solution and distilled for a short time, so that any volatile bases which may be present are expelled. The distillate is collected in a flask fitted with a Peligot tube containing dilute hydrochloric acid. When the distillate is evaporated to dryness, it leaves a crystalline residue ( $d=26\%$ ), which apparently contains ammonium chloride and methylamine hydrochloride. These two compounds can be separated by the François method<sup>9</sup>, as modified by Klein and Steiner<sup>4</sup>.

After distillation with barium hydroxide is complete, the distillation residue is acidified with dilute sulfuric acid and a few drops of hydrochloric acid, after which the excess sulfuric acid is completely eliminated by addition of barium hydroxide. The barium sulfate precipitate is filtered off with suction, and the filtrate is evaporated to dryness in a vacuum. This gives a nearly colorless crystalline residue (27 per cent), a part of which ( $e=15\%$ ) is soluble in absolute ethyl alcohol. The insoluble portion (12 per cent) is identifiable as a mixture of potassium chloride and sodium chloride.

#### IV. IDENTIFICATION OF ISOLATED FRACTIONS

A microchemical method has been developed by Klein, Krisch, Pollauf and Soos<sup>10</sup> which makes it possible to detect extremely small amounts of betaines (choline, glycine-betaine, trigonelline, nicotinic acid and stachydrine) in the presence of each other. This method utilizes eight reagents (Stanek's KI:I,  $HgCl_2$ ,  $PtCl_4$ ,  $PtI_4$ , Au chloride, bromide and iodide and KBi iodide). These are capable of forming characteristic crystals with betaines. This highly satisfactory method was as helpful as it was welcome in identifying all the separated fractions. To give a clear picture of its utility, we have been as liberal as possible in presenting photographs of the micropreparations.

*Fraction  $c_1$ .*—The precipitate of trigonelline hydrochloride ( $C_7H_7O_2N \cdot HCl$ ), which browns before decomposing at  $260^\circ C$ , gives with  $AuCl_3$  solution a yellow acicular precipitate, which, after crystallization from water, softens at  $181^\circ C$  and melts without decomposition at  $185-186^\circ C$ .

Analysis: Found 7.72% N; calculated for  
 $C_7H_7O_2N \cdot HCl$  8.07% N.

Trigonelline as the free base (colorless prisms from absolute alcohol) decomposes at  $220^\circ C$ .

Trigonelline can be completely identified by microchemical methods. Thus the hydrochloride gave these tests:

1.  $HgCl_2$ : characteristic aggregates of colorless rectangular rods.
2.  $PtCl_4$ : large yellow tetragonal and rectangular plates.
3.  $PtI_4$ : small black tetragonal or hexagonal parallelogram platelets or bundles of needles and irregular crystals. The latter two forms are chiefly noted near the edges of the preparation.

4.  $\text{AuCl}_3$ : long pale yellow needles aggregated in bundles.
5.  $\text{AuI}_3$ : rosettes of reddish brown rhombic platelets, frequently also with bundles of reddish brown needles.
6.  $\text{AuBr}_3$  golden brown filamentary crystals aggregated in bundles, some handsomely branched.
7. K Bi iodide: bright red to reddish brown prisms, aggregated in rosettes or bundles with scattered tetragonal or hexagonal yellowish brown platelets. Frequently in the same preparation very small red prisms lying close together, can also be detected.

Fraction  $c_2$  is apparently composed mainly of trigonelline hydrochloride. All the crystal forms characteristic of this compound can be obtained in the microchemical analysis.

Fraction  $c_3$ , as already stated<sup>7, 8</sup>, comprises a syrupy and a crystalline component. By digesting with purified anhydrous acetone, the syrupy component ( $c'_3=1\%$ ) can be removed. The insoluble crystalline component ( $c''_3=3\%$ ) comprises needles and hexagonal platelets. When completely dry, these crystals are not hygroscopic.

Fraction  $c_3$  yields micropreparations, which unmistakably disclose the presence of choline. This fraction gave the following tests:

1. Stanek's KI:I, yellowish brown to brown transparent oblique prisms, which may be intertwined with each other.
2.  $\text{HgCl}_2$ : skeletal aggregates of colorless needles, in feathery bundles.
3. Reinecke salt: clusters of nearly colorless, very fine filamentary or acicular crystals.

The crystalline fraction  $c'_3$  could not be identified, since it gave, with the above-mentioned Klein reagent, crystal forms widely different from the corresponding micropreparations of the most familiar betaines (glycine-betaine, trigonelline, stachydrine, choline, etc.). Thus it gave with:

1.  $\text{AuCl}_3$ : pale yellow fanlike clusters of needles or leaflets.
2.  $\text{AuBr}_3$ : brownish yellow to brownish red rosettes or bundles of long prisms or needles, which, by lateral growth, eventually yield the crystal form illustrated in Figure 9. Frequently the needles show fanlike branching at the ends.
3.  $\text{PtI}_4$ : black needles, frequently in regular star-like clusters.
4. KBi iodide: brownish red to red tetragonal and rectangular platelets, which may grow in fantastic patterns of aggregates if the solution is not too dilute.

It may also be noted that the aqueous solution of  $c'_3$  reacts distinctly acid to litmus. This property, in connection with the needles or hexagonal platelets, may indicate the presence of betonicine hydrochloride ( $\text{C}_7\text{H}_{13}\text{O}_3\text{N} \cdot \text{HCl}$ ) or its isomer, turicine hydrochloride, or both. As already stated, this cannot be established with certainty. (Unfortunately no more of either compound was available for verifying these micropreparations.) It did not seem worthwhile to carry out an extended and tedious analysis at this time.

Fraction  $d$ , as already stated, comprises a mixture of ammonium chloride and methylamine hydrochloride, which can be excellently separated by the Klein-Steiner modification<sup>4</sup> of the François method<sup>9</sup>. This method (for details, see the original publications, and Winterstein<sup>11</sup>) depends on the ability of yellow mercuric oxide to add ammonia quantitatively, with formation of ammonium mercuric oxide. With alkylamines, on the other hand, mercuric oxide does not react. By

separate treatment of the precipitate, containing excess mercuric oxide and the ammonium double compound, and the solution of alkylamine, it was possible to show that fraction *d* (26 per cent) is mainly ammonium chloride (22 per cent) with only a small proportion of methylamine hydrochloride (4 per cent). According to Klein and Steiner<sup>1</sup>, methylamine hydrochloride can be identified microchemically with the aid of 2,4-dinitro-1-naphthol, prepared as described by Morgan and Evans<sup>12</sup>.

*Fraction e.*—Microscopic analysis of the dried preparation indicates the presence of colorless prisms, together with leaflets or flakes of extremely fine needles (the main component), readily discernible under a polarization microscope. Microchemical analysis by the Klein method (see below) indicated that this fraction still contains traces of trigonelline hydrochloride. By digesting the thoroughly dried fraction *e* for a short time with a little absolute ethyl alcohol, the flaky clusters of needles can be largely eliminated (9 per cent). The insoluble residue gives crystal forms with the designated microchemical reagents as follows:

1.  $\text{AuBr}_3$ : reddish brown tetragonal or hexagonal platelets or prisms, often combined in rosettes of three, four or more crystals. Along with these forms golden brown intertwined filamentary crystals may be observed. This indicates the presence of trigonelline.

2.  $\text{PtI}_4$ : dark brown to black tetragonal rectangular or much more rarely hexagonal platelets.

3.  $\text{KBi}$  iodide: brownish red to black tetragonal oblique prisms, clustered in rosettes of four or six crystals, or in T or F shape. Star-shaped aggregates may be seen in the same preparation.

These micropreparations agree very well with those obtained by Klein with stachydrine ( $\text{C}_7\text{H}_{13}\text{O}_2\text{N} \cdot \text{HCl}$ ). The presence of these betaines could not be confirmed by any other method.

The flaky clusters of needles are highly hygroscopic, and could not be identified microchemically, since they give amorphous precipitates with Klein's reagent. When the base is liberated from the hydrochloride, the piperidine odor is very strong. The flavianate crystallizes in yellow needles or filaments, which begin to sinter at 235° C and decompose at 247-248° C.

From this investigation, which makes no claim to completeness, it may be concluded that fresh latex contains nitrogenous bases which are comparatively easy to isolate in the form of their hydrochlorides. The mixture of hydrochlorides, of which latex contains an average of 650 mg. per liter, appears to have approximately the composition: trigonelline hydrochloride 35-37, ammonium chloride 22, potassium chloride and sodium chloride 12, methylamine hydrochloride 4, and choline hydrochloride 1 per cent.

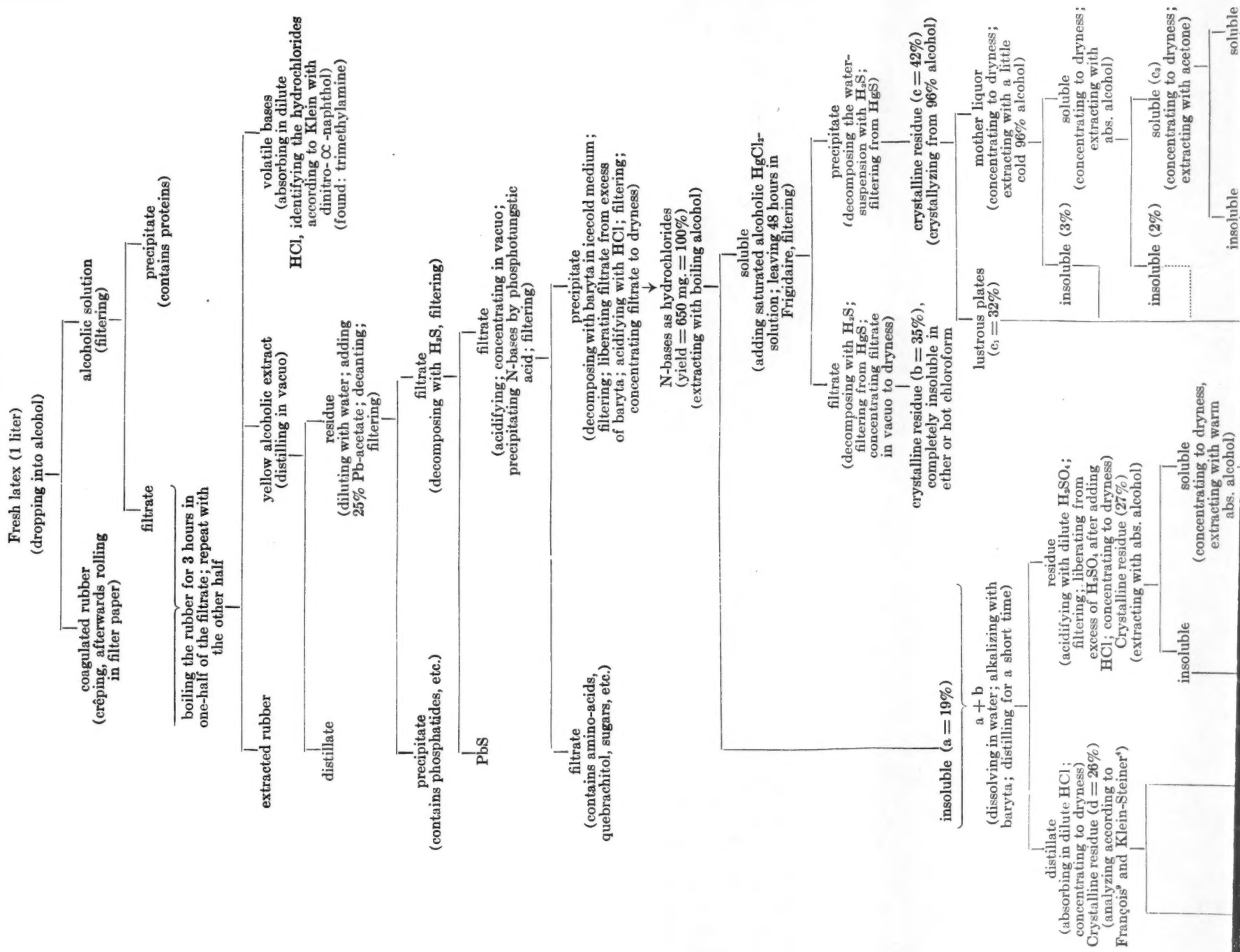
A small amount of stachydrine hydrochloride was always detected in this mixture, although its amount could not be ascertained, since it probably also contained betonicine and (or) turicine hydrochloride. Finally it was established that the mixture contains 9 per cent of lustrous leaflets, from which a flavianate decomposing at 247-248° C could be obtained.

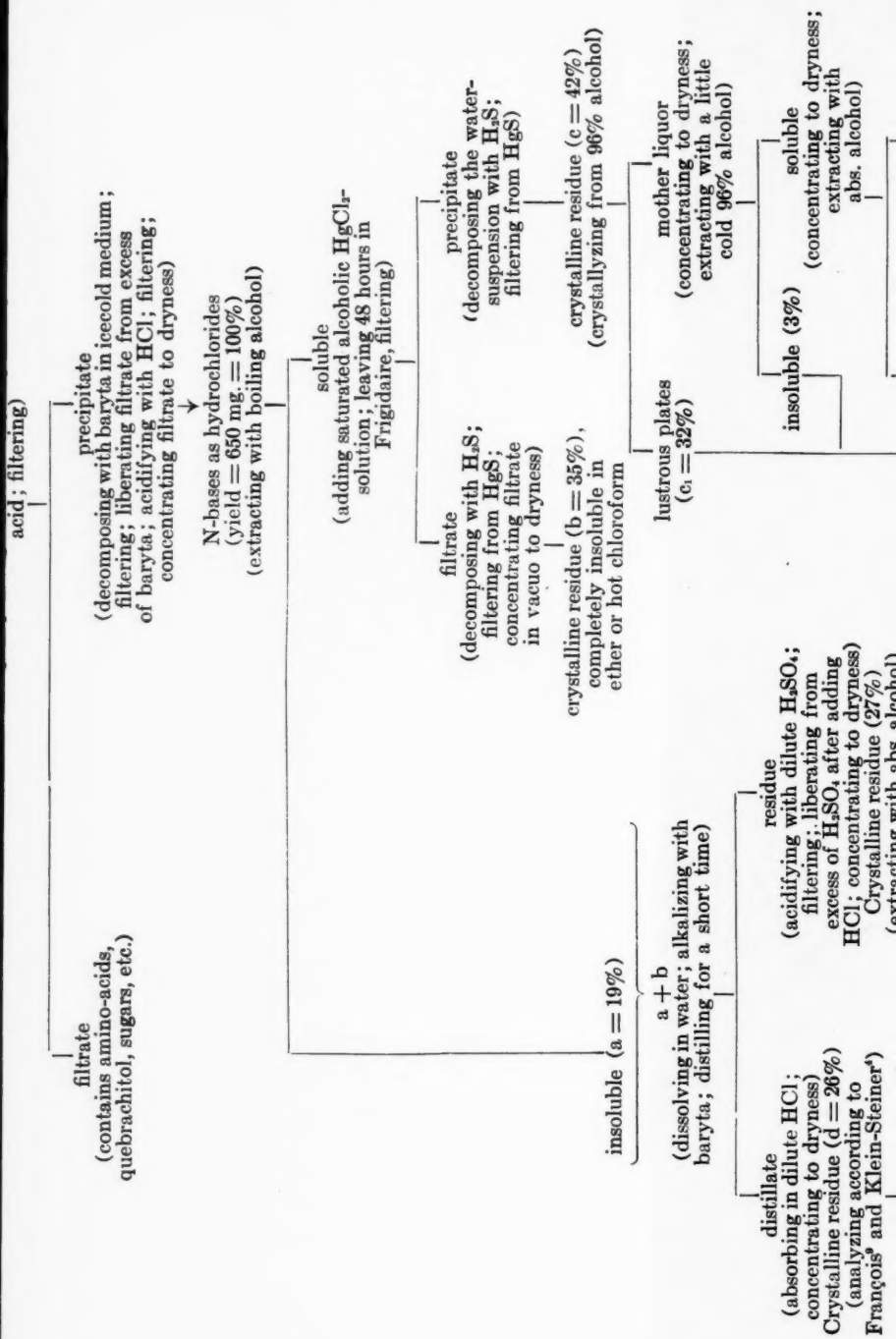
Although this leaves about 25 per cent of the mixture unidentified, we feel it is necessary to be satisfied with this result for the present. As soon as opportunity offers, a supplementary investigation will be made.

## V. SUMMARY

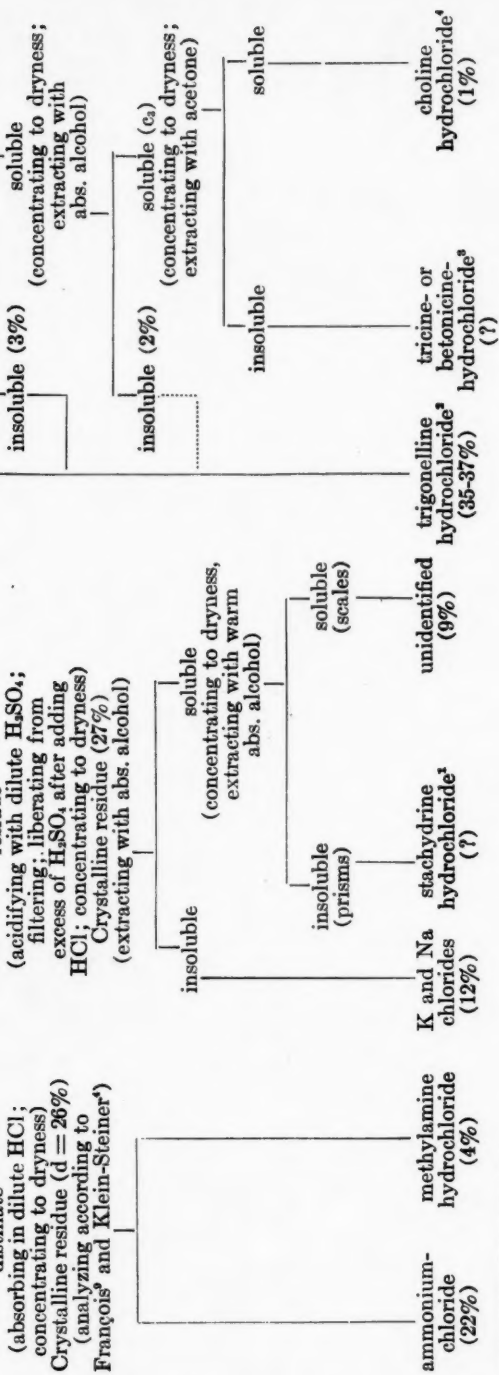
This paper describes a method for isolating and identifying nitrogen bases, *e.g.*, ammonia, amines and betaines, present in fresh unammoniated latex. The

SCHEME OF THE ADOPTED METHOD FOR THE ANALYSIS OF NITROGEN BASES

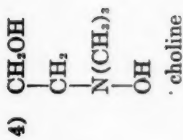
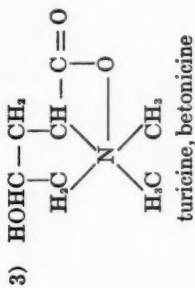
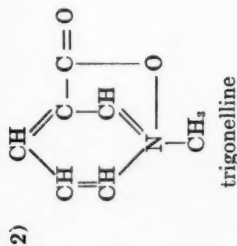
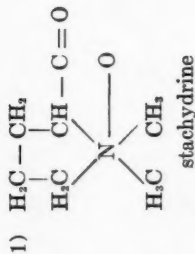








Formulas:





outline above summarizes the results. The method does not claim perfection. The author wishes to emphasize that the percentages recorded in the outline are not exact, and are given only to indicate the proportions of the respective fractions.

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# ORGANIC ANALYSIS OF HEVEA LATEX. VI

## ALKALOIDS IN WHOLE-LATEX RUBBER \*

R. F. A. ALTMAN

### I. INTRODUCTION

The question arose as to whether latex contains free nitrogen compounds other than the amino acids<sup>1</sup>, amines and betaines<sup>2</sup> which had previously been isolated. It seemed worthwhile to investigate the presence of alkaloids, especially since there is no information on this subject in the literature. A preliminary test indicated that alkaloids do, in fact, occur in latex or, at least, a substance can be separated which gives precipitates with the usual alkaloid reagents.

### II. OUTLINE OF THE INVESTIGATION

Since the method of Stas-Otto<sup>3</sup>, employed for separating alkaloids, is a familiar one, we shall merely outline the investigation here. The material consisted of 2 kg. of finely divided whole-latex rubber. (Meantime a more suitable material for separating alkaloids from *Hevea* latex by the Stas-Otto method has been found. We hope to return to this subject later). The rubber was sheeted by pouring about 5 liters of latex in a very thin layer onto glass plates and drying in air at room temperature. The entire quantity was worked up in 400 gram lots.

The general alkaloid tests, together with certain color tests, were carried out with the various extracts (italicized in the outline). The results of these tests are summarized in the table below, which also includes the results of the Lassaigne test on the acid ether extract and on alkaline ether extract II.

As for the last named extract, evaporation yielded only 6.8 mg. of a brown, extremely bitter syrup, mixed with a few crystals.

From this discussion it may be concluded that alkaloid-like substances occur in *Hevea* latex, although in extremely small proportions. For the present, at least, it does not seem particularly urgent to work up large quantities of whole latex rubber merely to permit identification of the alkaloids (the first extracts for such a program would be the acid ether extract, alkaline ether extract II, and amyl alcohol extract; see the table).

### III. SUMMARY

The Stas-Otto method makes it possible to separate from whole-latex rubber very small quantities of bitter substances which give the usual alkaloid tests and some color reactions (see table below).

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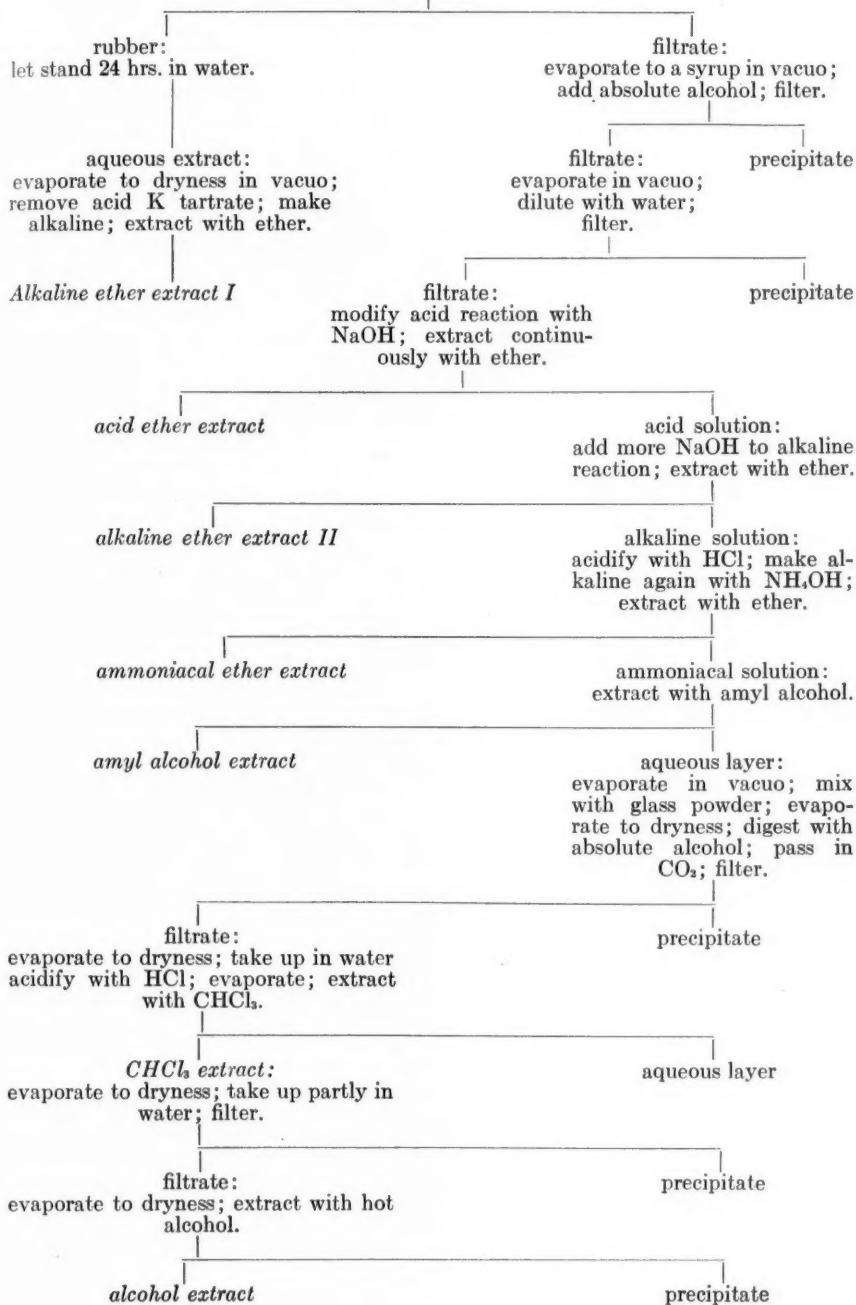
<sup>1</sup> Altman, *Arch. Rubbercultuur* **24**, 642 (1940).

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\* Translated by Julian F. Smith for RUBBER CHEMISTRY AND TECHNOLOGY from Mededeeling No. 28 van de Afdeling Rubber Research van het Proefstation West Java, Buitenzorg, Java. Also published in *Archief voor de Rubbercultuur* **28**, No. 1, pp. 14-17 (1941).

400 grams of whole-latex rubber:  
digest with 2000 cc. of 0.3% alcoholic tartaric acid solution  
(pH  $\pm$  3) overnight at 80° C; cool; filter with suction; wash  
with alcohol.



	Nitrogen (detected according to Lassaigne)	Alkaloid reactions						Color reactions				
		I—KI (Bouchardat)	K <sub>2</sub> HgI <sub>4</sub> (Mayer)	Picric acid	Tannin	Phosphotungstic acid (De Vrij-Sonnenschein)	Mercuric chloride	H <sub>2</sub> SO <sub>4</sub> + HNO <sub>3</sub> (Brdmann)	H <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> MoO <sub>4</sub> (Froehde)	H <sub>2</sub> SO <sub>4</sub> + HCOH (Marquis)	H <sub>2</sub> SO <sub>4</sub> + vanillin (Van Itallie-Steenhauer)	Sulfuric acid
Fractions possibly containing alkaloids (for the analysis of whole latex rubber by the method of Stas-Otto)												
Alkaloid ether extract I . . . . .		+	+	+	+	+	+	red brown	yellowish brown to yellow	yellowish brown	brown	brown
Acid ether extract . . . . .	+	+	+	+	+	+	+	red brown	brown to yellow	brown	brown	brown
Alkaloid ether extract II . . . . .	+	+	+	+	+	+	+	red brown	brown to yellow	brown	dirty-violet to red-brown	brown
Ammoniacal ether extract . . . . .		+	+	+	+	+	+	brownish	brownish to yellow	brownish	brown	brownish
Amyl alcohol extract . . . . .		+	+	+	+	+	+	red brown	brown to yellow	brown	brown	brown
Chloroform extract . . . . .		+	+	+	+	+	+	brownish	brownish to yellow	brownish	brown	brownish
Alcohol extract . . . . .		+	+	+	+	+	+	brownish	brownish to yellow	brownish	brown	brownish



# EFFECT OF STRAIN ON THE AGING OF VULCANIZED RUBBER \*

T. R. DAWSON and J. R. SCOTT

**INTRODUCTION.**—Vulcanized rubber which is stored in a state of strain deteriorates much more rapidly than similar rubber not under strain. This observation has immediate application to rubber goods of many kinds, such as tire tubes packed in a folded state, tires standing under strains due to their own weight or to that of the vehicle, coiled and bent cable and hose, football bladders and bathing caps packed flat, folding-boat covers, and so on.

There has been a moderate amount of investigation devoted to this phenomenon in the last two decades<sup>1</sup>, but, in the main, quantitative studies have been devoted to simply stretched rubber, and data on the effects of folds or creases have not been available. As folds and creases involve compression as well as stretching, it cannot be assumed that conclusions drawn from studies of stretched rubber are applicable without change to rubber articles subjected to folding or creasing.

The observations given in the present paper, made on different occasions in connection with other work, bring together several examples of the effect of folds on the aging of rubber.

**SERIES I.**—Flat sheets between two and three mm. thick were prepared from a red stock, available in quantity from other work. This mixture comprised smoked sheet, 80 parts; crimson antimony sulfide (containing free sulfur), 20 parts.

The sheets were vulcanized for 60 minutes at 153° C, a period corresponding to one-third more than that to optimum tensile properties, with a view to hastening aging changes.

A first series of tensile tests was made 24 hours after vulcanization, and the remainder of the rubber put out in the open air as follows:

(1) *Unstretched.*—A group of rings was strung on a mandrel small enough to carry them without tension.

(2) *Stretched.*—A second group was strung on a mandrel improvised from sheet aluminum of such a size as to stretch the rings approximately 20 per cent.

(3) *Unbent.*—Pairs of square pieces were loosely clipped together at their upper edges and suspended by the clips.

(4) *Bent.*—Single square pieces were folded across the middle parallel to a pair of opposite edges, and held by clips at the ends and centre of the fold (to avoid gripping it at places where ring-cuts would subsequently cross the fold).

With these arrangements the rings, whether stretched or unstretched, and the squares, whether bent or unbent, exposed about the same amounts of surface to the weather in each case. Tensile tests were made periodically, Schopper rings being cut from the squares with the fold running approximately along a diameter of the ring.

The period of exposure, from September 8 to October 26, included a number of warm days and much sunshine during the first half of the period. The following observations on the appearances of the test-pieces form evidence of changes which took place.

\* Reprinted from *Transactions of the Institution of the Rubber Industry*, Vol. 16, No. 4, pages 198-210, December 1940.

Sept. 8. Exposure commenced.

Sept. 14. Stretched rings showed faint surface cracks all over exposed parts and the bent squares along the outside of folds. The faint cracks became pronounced on slightly extending the specimens. The untensioned pieces remained smooth.

Sept. 23. Cracking of the tensioned specimens was more evident. Unstressed rubbers were still sound.

TABLE I

UNSTRETCHED RINGS					
Date of test	Breaking load (kg. per sq. mm.)	Elongation (per cent)		Rigidity (kg. per sq. mm. at 300 per cent elongation)	Permanent set (per cent after 300 per cent elongation)
		Break	0.5 kg. per sq. mm.		
Sept. 8					
10 a.m. ....	1.19	774	623	0.138	1.2
5 p.m. ....	0.76	716	627	0.137	1.45
Sept. 11 ....	1.05	750	615	0.144	1.45
Sept. 14 ....	0.83	720	608	0.143	1.7
Oct. 1 ....	0.87	720	605	0.148	2.4
Oct. 10 ....	0.68	664	598	0.147	2.9
Oct. 26 ....	0.61	657	593	0.154	2.8
STRETCHED RINGS					
Sept. 8					
10 a.m. ....	1.19	774	623	0.138	1.2
5 p.m. ....	0.91	750	627	0.135	1.1
Sept. 11 ....	0.67	691	620	0.138	1.1
Sept. 14 ....	0.73	736	643	0.122	1.0
Oct. 1 ....	0.47	645	—	0.125	1.45
Oct. 10 ....	0.51	650	645	0.121	1.2
Oct. 26 ....	0.14	366	—	0.116	1.7
UNBENT SQUARES					
Sept. 8	1.19	774	623	0.138	1.2
Sept. 11	0.74	701	617	0.140	1.45
Sept. 14	0.84	722	608	0.143	1.7
Oct. 1	0.17	348	—	0.148	1.65
Oct. 10	0.28	449	—	0.142	1.75
Oct. 26	0.60	657	597	0.146	2.9
BENT SQUARES					
Sept. 8	1.19	774	623	0.138	1.2
Sept. 11	0.88	738	614	0.148	1.2
Sept. 14	0.65	670	614	0.135	1.7
Oct. 1	0.99	745	606	0.147	1.95
Oct. 10	0.78	701	613	0.136	1.95
Oct. 26	0.45	584	—	0.146	1.95

Oct. 1. Cracking was now marked in the stressed rings and squares, and faint signs of cracking developed in the unstressed rings. The flat squares remained smooth.

Oct. 26. The stressed rubbers displayed deep large cracks, and surface cracking of the unstressed rings was more obvious. The flat squares remained without visible cracks to the end of the exposure.

Table I gives the tensile tests. All elongations are expressed as percentages of the initial length of a Schopper ring, and not as functions of the length deformed

by exposure to stress. The permanent set after 300 per cent elongation is also referred to the initial ring length, but is the amount of set obtained additional to set occurring during exposure.

The two sets of results on the squares, bent and unbent, show surprisingly small differences. The breaking loads vary fortuitously, but are definitely diminishing after a month's exposure. The elongations at fixed load show signs of diminishing, rigidities increase, and the set after constant elongation increases. These tests agree reasonably well with one another for bent and unbent specimens. The occurrence of two small zones of cracks on a Schopper ring has evidently had little effect on the tensile tests in these experiments.

On the other hand, in the figures for stretched and unstretched rings, the effects of tension are clearly seen. The breaking load falls off in both series, but more quickly and to a greater extent in the stretched group. The elasticity diminishes and the rigidity increases normally in the unstressed samples, but exactly the reverse takes place in the stressed rings. The permanent set after constant elongation increases appreciably in the stressed samples, but falls to a minimum and then rises in the stressed series.

Complementary to the set tests on the stretched rings, the results in Table II show the amount of set developed by the exposure. The measurements were made

TABLE II

Date .....	Sept. 8	Sept. 8	Sept. 11	Sept. 14	Oct. 1	Oct. 10	Oct. 26
	10 a.m.	5 p.m.					
Set (per cent) ..	0.0	0.85	1.93	2.42	3.38	4.84	6.29

10 minutes after releasing the stretched rings, and the set is expressed as a percentage of the initial length of the Schopper ring.

The rings cut from the folded squares showed a negligible amount of set due to folding, but acquired a distortion which was still visible a year later.

The general weakening of the rubber under tension is clearly demonstrated in the tests on the rings. It seems questionable, however, whether the actual cracks on the surface indicate unusually quick oxidation, or arise simply from mechanical shearing.

SERIES II.—Four  $30 \times 3\frac{1}{2}$  motor inner tubes made by different manufacturers, denoted by the letters A, B, C, and D, were used for these experiments. These tubes were the same as those used in the aging investigation on inner tubes previously described<sup>2</sup>. Ring specimens were prepared by mounting a section of the tube on a wooden mandrel, rotating this in a lathe, and cutting off the rings with a sharp knife. The thickness (distance between the plane faces) of the rings was 3 mm., the width being equal to the wall thickness of the tube, *viz.*, 2 to 3 mm. To determine the effect of folding on aging, some of the rings were aged without being folded, and some with a fold produced by gripping the ring between the wooden jaws, about 1 cm. wide, of a spring clip to produce a more or less sharp fold as shown at F, see Figure 1. Two sets of folded rings were tested, one having  $d=0.5$  cm. ("sharp fold") and the other  $d=1.0$  cm. ("loose fold"). The unfolded rings were supported on glass tubes 4 cm. in diameter.

The rings were aged in a Geer oven at 70° C, and tensile tests made on a Schopper machine after various aging periods. Each test after aging was made on two rings. The average tensile strength results are shown plotted against aging period in Figure 1.

The fall in tensile strength was accelerated by folding, especially when the fold was acute. This is more clearly shown by comparing the aging periods required to reduce the tensile strength to 50 per cent of its initial value (see Table III).

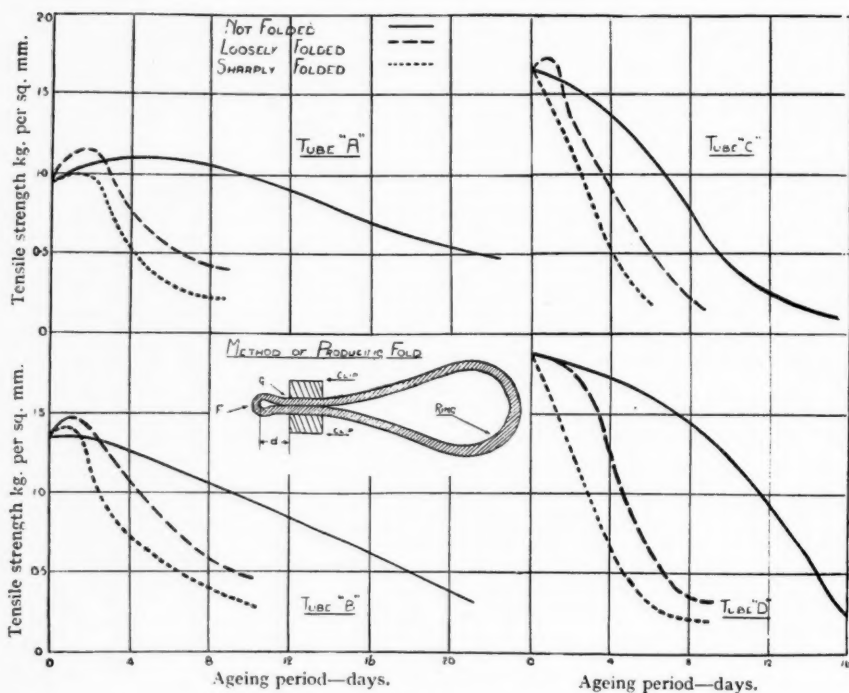


FIG. 1.

TABLE III

Tube	A	B	C	D
Aging period (days) to 50 per cent tensile strength				
Unfolded .....	22.5	15.0	7.5	12.0
Loosely folded .....	7.5	7.0	4.3	5.0
Sharply folded .....	4.5	4.5	3.0	3.2
Per cent increase in rate of deterioration				
Loosely folded .....	195	110	75	140
Sharply folded .....	390	230	150	270

The reciprocals of the aging periods to 50 per cent tensile strength represent the relative rates of deterioration. The extent to which this rate was increased by folding is shown in the lower part of Table III. These figures indicate that the sharp fold produced twice as great an effect in accelerating deterioration as the loose fold. They show also that the four tubes were affected to different extents by folding.

As tube A, which had the best aging properties under normal conditions, was affected most, and C, with the worst aging properties, was affected least, folding

tended to equalize the rates of deterioration of the four tubes, as is evident also from the figures in the upper part of Table III. Taking the four tubes as a whole, however, the susceptibility to folding did not appear to bear any close relationship to rate of deterioration under normal conditions, or to the extensibility or permanent set of the rubber, *i.e.*, the two properties which largely determine the stresses set up at the fold and the extent of permanent deformation produced. This is shown by arranging the tubes in order according to each property:

Effect of folding		Rate of deterioration		Permanent set after 400 per cent elongation		Elongation at 0.15 kg. per sq. mm.	
Greatest:	A.	Least:	A.	Greatest:	B.	Least:	B.
	D.		B.		A.		C.
	B.		D.		C.		D.
Least:	C.	Greatest:	C.	Least:	D.	Greatest:	A.

During the accelerated aging test, the folded part of the ring stiffened much more than the rest and became set in a sharply curved form, so that on removing the clip the fold did not straighten out. After 6 days' aging, all the sharply folded rings showed cracks on the inside of the fold when this was opened out slightly; no cracks developed on the outside where the rubber was subjected to extension. No cracks were observed on the loosely folded rings, and there were no marked differences between the four tubes in regard to severity of cracking.

TABLE IV  
POSITION OF BREAK

F = broke at fold (F in Figure 1).  
P = broke at fold formed by packing the tube (this was present only in A).  
G = broke at point where folded portion emerged from grip (G in Figure 1).  
L = loose fold; S = sharp fold.

Tube Days aging	A		B		C		D	
	L	S	L	S	L	S	L	S
1.....	P	P	G	F	—	F	—	F
2.....	P	F	F	F	F	F	F	F
4.....	F	F	F	F	F	F	F	F
6.....	F	F	G	F	F	F	F	F
9.....	F	F	F	F	F	F	F	F

The occurrence of cracking on the inside of the fold shows only that in these experiments compression had a greater effect than extension in accelerating hardening and deterioration of the rubber, and this same result has been observed in other cases. It would be of great interest to know whether this is due to compression having a greater tendency to promote changes in the structure of the rubber, *e.g.*, the growth of a microcrystalline structure.

Practically all the aged rings, when subjected to tensile tests, broke at the fold, showing clearly that this was a point of weakness (see Table IV).

SERIES III.—These observations relate to a series of eleven  $32 \times 4\frac{1}{2}$  motor tubes on which tensile tests were made, using rings cut on the lathe as described in Series II. These tubes had been stored, folded in cardboard boxes in the usual manner, for about 5 months after purchase before the tests were made. During this period many of the tubes had become "set" in a flattened form, so that the rings cut from them on the lathe had more or less sharp bends at two opposite points. The acuteness of the bend varied, as shown in Table VI, from "slight"

(which merely gave the ring a somewhat elliptical shape) to "acute," where the ring was bent to an internal radius of about 6 mm. In some cases the rubber showed signs of cracking on the inside of the bend. In general the rings with more or less acute bends broke at the bend when subjected to tensile tests (see Table VI). The fold produced during storage was thus clearly a point of weakness.

To find out the extent to which folding weakened the rings, the tensile strength figures in column (a) of Table V may be compared with those determined on Schopper rings punched from the tube in such a position as to avoid the fold.

TABLE V

Tube	(a) Tensile strength (kg. per sq. mm.)	(b) Elongation at break (per cent)	(c) Variation of tensile strength (per cent)	(d) Corrected tensile strength (kg. per sq. mm.)
F .....	0.60	642	92	1.24
H .....	1.51	716	60	1.74
J .....	1.29	869	21	1.20
K .....	1.54	771	13	1.56
L .....	1.32	678	28	1.72
M .....	1.73	677	37	2.19
N .....	0.88	601	86	1.48
P .....	1.33	758	30	1.34
Q .....	1.30	604	35	1.73
R .....	1.71	755	36	1.80
S .....	1.55	744	16	1.57

## Notes:

Columns (a) and (b): Determined on lathe-cut rings; each figure is an average for 9 rings.

Column (c): Difference between highest and lowest figures for the 9 lathe-cut rings; expressed as percentage of mean.

Column (d): Punched rings, avoiding folds.

TABLE VI

Tube	Acuteness of bend	Cracking	Position of break
F	Acute	Slight	All at bend
H	Moderate	Trace	All at thinnest part of ring*
J	Moderate	None	No definite position
K	Slight	None	No definite position
L	Fairly acute	Trace	75 per cent broke at bend
M	Moderate	Trace	75 per cent broke at or very near bend
N	Acute	Slight	All at bend
P	Slight	None	No definite position
Q	Fairly acute	Slight	50 per cent at bend, 50 per cent at thinnest place*
R	Moderate	None	No definite position
S	Slight	None	Mostly about 1 in. from bend

\* Note: These tubes showed marked irregularity in thickness.

In making this comparison it must be noted that the greater ratio of width to diameter of the punched rings tends to make them give lower results. Theoretically the tensile strengths of Schopper rings should be increased by about 14 per cent for rubbers which give stress-strain curves of the type under consideration. The figures thus increased are given under "Corrected Tensile Strength" in Table V, for comparison with the figures for lathe-cut rings.

Comparison of the figures in columns (a) and (d) of Table V shows that J, K, P, R, and S were not markedly affected by folding, whereas F, H, L, M, N, and Q were weakened, this effect being large with F and N, which had the most acute folds. The correlation between acuteness of folding, cracking at the fold, and



lowering of tensile strength by folding is more clearly shown by arranging the tubes in order according to each property (see Table VII). It would be expected that rings weakened by folding would give more erratic tensile strength results than those not so affected. The figures given in Table V, column (c), show the extent of variation of tensile strength between different parts of the tube, and in the last column of Table VII the tubes are arranged in order according to the magnitude of this variation.

It is clear that tubes F and N suffered most by being stored in a folded condition; H, L, M, and Q were affected less, and J, K, P, R, and S hardly at all.

*Folding during accelerated aging.*—The effect of maintaining a sharp fold or bend in the test ring during Geer aging has already been described, in the case of 4 tubes, in Series II above.

A similar set of experiments has been made with the present tubes. For this purpose Schopper rings were held, as shown in Figure 2, between 2 strips of wood

TABLE VII

	Acuteness of folding	Cracking	Lowering of tensile strength	Irregularity of tensile strength
Most	FN	FNQ	F	F
	LQ		N	N
			Q	
		HLM	L	H
	HJMR		M	MRQ
			H	LP
			R	
	KPS	JKPRS	KPS	JKS
Least			J	

TABLE VIII

Tube .....	F	H	J	K	L	M	N	P	Q	R	S
Ratio .....	3.0	2.5	1.9	2.6	2.5	2.4	2.25	2.0	2.6	2.2	1.9

A, A, about 30 mm. wide, so as to leave a projecting "loop" B at each side, the internal radius of the loop being 5 to 6 mm. In the previous experiments this radius was made much smaller, but the larger radius is preferable, as it is nearer to the conditions met in storage. The rings, thus held between the strips, were aged in a Geer oven, one ring being tested after each of 8 aging periods (only 8 rings could be obtained from the material available).

The aging curves are shown in Figure 2, which shows that folded rings deteriorated more rapidly than unfolded ones. The fact that almost all folded rings broke at the fold showed that this was responsible for the accelerated deterioration.

The approximate ratio between the rates of deterioration of folded and unfolded rings is given in Table VIII.

These ratios are to some extent affected by the fact that the unfolded rings, which were tested as part of another investigation, were cut from pieces of tubes after these had been aged, so that, during aging, a smaller surface was exposed to oxidation than in the case of the folded rings. According to other results obtained in these laboratories, the ratios in Table VIII should be reduced by about 10 per cent to correct for this.

It might be expected that the tubes showing the highest ratios would be those which had their tensile strength lowered most by being stored folded (see Table

VII). The orders in which the tubes are arranged by these two properties have accordingly been compared in Table IX.

TABLE IX

	Lowering of tensile strength in storage	Ratio from Table VIII
Greatest:	F N Q L M H R KPS	F KQ HL M N R P JS
Least:	J	JS

With the exception of H, K, and N, the two orders are almost the same, and it is possible that the apparent exceptions may be due to experimental errors, as the number of rings available for the aging tests was small.

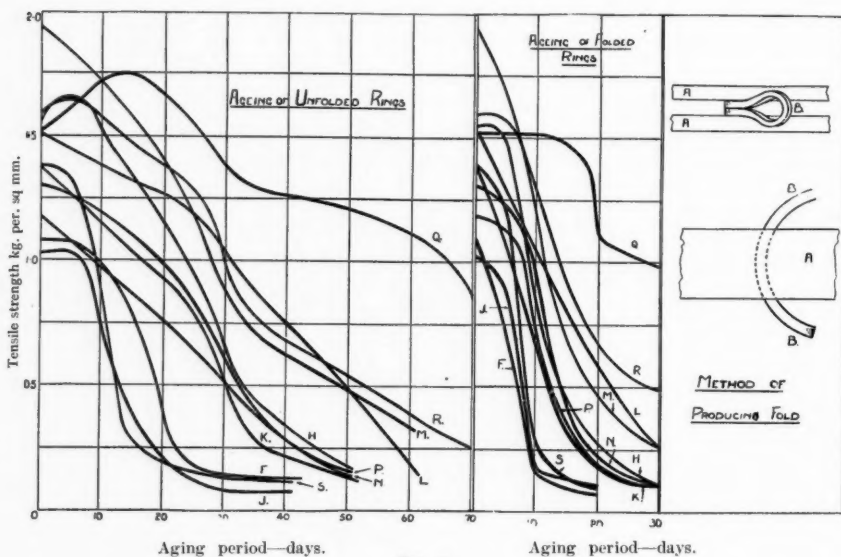


FIG. 2.

*Mechanism of the effect of folding.*—A ring kept for some time with a sharp fold may have its tensile strength (determined on the Schopper machine) lowered in one or both of two ways:

(1) The bend sets up stresses in the rubber, and these, according to the generally accepted view, hasten deterioration. If the rubber is one which tends to acquire permanently any deformation to which it is subjected, it might be expected to “flow” at the bend in such a way as to relieve the stresses and so to lessen the harmful effect of the bend.

(2) If the rubber “flows”, as suggested above, it will give the ring a sharp permanent curvature at the bend, and the length of the inner surface of the bent

portion will thus be made less than the mean length of that portion. When the ring is straightened out in the tensile test the inner surface will be subjected to a greater percentage elongation than the rest of the ring, and will therefore presumably break first, thus causing abnormally low tensile strength and breaking elongation readings. Taking the mean stress-strain curve of the 11 tubes, with a tensile strength of 1.6 kg. per sq. mm. and a breaking elongation of 770 per cent, it can be shown that if a ring 2.8 mm. wide (the mean for the 11 tubes) acquires a permanent bend of internal radius 6 mm., as actually happened during storage of some of the tubes, the ring would break at a stress of only 0.8 kg. per sq. mm. and an elongation of 610 per cent.

It is thus evident that a tendency to "flow" may act in either or both of two opposite ways. It might be expected that permanent set tests would indicate the tendency of the rubber to flow but, with the present group of tubes, there is no distinct relationship between set after constant elongation and the acuteness of the permanent bend formed during storage. It appears, therefore, that some other test is required to measure "flow", and in this connection prolonged compression tests<sup>3</sup> might prove useful. Under these circumstances it is hardly to be expected that permanent set after constant elongation would be closely related to the effects of folding on tensile strength, and actually no such relationship is found, either in the present experiments or those described in Series II.

The two effects described under (1) and (2) above would appear to be of very different importance in relation to a tube subsequently put into use. Effect (1) produces a strip of partly perished, and therefore weak, rubber running along each side of the tube. Effect (2), however, merely produces, on the inside of the fold, a local increase in the strain caused by inflation of the tube; thus, if the bulk of the tube were stretched 10 per cent, the local strain at the fold, in the numerical case considered in paragraph (2), would be about 35 per cent. This might possibly have a greater accelerating effect on deterioration than the 10 per cent in the rest of the tube but, on the other hand, as the tube has acquired a permanent fold when kept folded, there is no reason to believe that it would not become permanently straightened when kept inflated inside a tire cover, and so eliminate the excess strain at the fold.

It would be of interest to know to what extents the two effects described under (1) and (2) come into play during storage in a folded condition. The fact that a considerable loss of tensile strength in lathe-cut rings usually accompanies a sharp permanent fold (Table VII) shows that the second effect, due to shortening of the inner circumference, is present to an important extent. If this were the only effect involved, the tensile strength, determined on a narrow straight test-piece cut along the fold, should be normal whereas, if the first-named effect, acceleration of perishing by the stresses at the fold were alone present, such a test-piece would give about the same results as a lathe-cut ring. To settle this point, some experiments were made with the three tubes most affected by folding. Dumbbell test-pieces were used, with the narrow central portion (6 mm. wide) running along the fold. Only 2 test-pieces could be obtained from tubes N and Q and one from F; another test-piece from a tube (FF) of the same make as F was included because this tube also gave low tensile strength figures when tested by lathe-cut rings. As dumbbells should theoretically have higher tensile strengths than rings, and lathe-cut rings higher tensile strengths than punched rings, approximate corrections have been applied to reduce all the figures to the basis of lathe-cut rings (see Table X).

So far as these scanty results go, they show that, with Q, the stresses set up by folding have not greatly hastened deterioration, whereas with F, FF, and N

this effect has occurred. The fact that tubes J, K, P, R, and S have not been appreciably weakened at the fold during storage (Table V) shows, however, that the influence of these stresses is not always serious.

**SUMMARY.**—A fold maintained in rubber tensile-test rings during Geer aging greatly accelerates the fall in tensile strength. A similar effect is produced by storing rubber articles in a closely folded condition at room temperature, the fold becoming a line of weakness. Thus, in a series of tire inner tubes that had been kept packed in cardboard boxes for 5 months, the tensile strength of specimens cut across the fold was as much as 50 per cent lower than that of the unfolded part.

Among eleven inner tubes of different makes, the weakening at the fold produced by storage was generally greater, the greater the harmful effect of folding in Geer aging. As, however, there were a few exceptions, it is not certain that Geer tests on folded rings would always correctly indicate the tendency of a tube to be damaged by folding.

TABLE X  
TENSILE STRENGTH (KG. PER SQ. MM.) WITH VARIOUS TYPES  
OF TEST-PIECE

	F	FF	N	Q
Dumbbell.....	0.71*	0.88*	1.25	1.65
Lathe-cut rings .....	0.60	0.71	0.89	1.30
Punched rings .....	1.24	—	1.48	1.73

\* The test-piece broke in the grips, so that the true tensile strength is probably higher than that given.

In some cases the tubes stored in a folded condition showed cracks on the inside of the old, but not on the outside.

In outdoor exposure tests lasting 7 weeks, folding produced much less effect on the fall in tensile strength than did direct extension of 20 per cent.

It is shown that two main factors may be involved in the mechanism of the weakening effect of folding, *viz.*, the stresses set up at the fold, and the "flow" of the rubber. Experiments indicate that "flow" occurs in a widely varying degree, and that the stress factor appears to be present in some cases but not in others. Measurements of permanent set after constant elongation do not show quantitatively the tendency of the rubber to "flow" or to be weakened by folding.

The authors wish to thank the Council of the Research Association of British Rubber Manufacturers for permission to publish this paper.

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# THERMAL PROBLEMS IN RUBBER MANUFACTURE \*

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## I. INTRODUCTION

Vulcanization, the basic process of the whole rubber industry, is so dependent on temperature that it was named after Vulcan, the God of Fire. Because of the low conductivity of rubber compounds, it is often difficult to heat uniformly the large complex rubber parts required by modern civilization. However, careful studies of the thermal problems involved and the development of "flat-curing" compounds have made possible satisfactory vulcanization of articles ranging in size from one-gram toy tires to enormous "earth-mover" tires weighing more than a ton, or from hundredth-inch diameter thread to massive railroad car springs over a foot in diameter, or even the vulcanization of rubber linings on the large areas inside 10,000-gallon tank cars.

Other heat problems occur in the processing of rubber preparatory to vulcanization. Large quantities of heat are generated by the mechanical working of the plastic masses during mastication, mixing, extrusion or calendering. In most cases this heat must be removed to prevent excessive temperature rise.

Finally, heat problems may be encountered after the fully vulcanized products enter the customer's service. Heat is developed when rubber is subjected to rapid flexure because of its imperfect elasticity, and the low conductivity prevents ready escape of the heat. Such problems are solved by reduction of hysteresis in rubber compounds, and by proper choice and assembly of structural elements for reduction of internal friction and improvement of cooling.

## II. THERMAL CONDUCTIVITY AND DIFFUSIVITY OF RUBBER

The thermal conductivity of crude rubber has an average value of 0.000375 cal./ (sec.) (cm<sup>2</sup>) (°C/cm). While most of the materials which must be added to crude rubber to give it satisfactory physical properties have somewhat higher conductivities than rubber itself, practical rubber compounds will rarely have as much as two times the conductivity of rubber. The conductivity of rubber is very low, about that of white pine wood, a material once used as an insulator on steam-engine cylinders. It is only about three times as great as that of common porous insulators such as cork-board or rock wool, and it is less than 1/200 as much as that of common metals.

Rubber has not only a low conductivity but also a relatively high specific heat, about 0.48. This makes its volumetric heat capacity about the same as that of metals. Consequently its thermal diffusivity, or ratio of thermal conductivity to volumetric heat capacity, is very low. Thermal diffusivity is a measure of the rate of temperature propagation through a material. The diffusivity of rubber compounds usually lies between 0.0008 and 0.0014 c.g.s. unit as compared with about 0.0015 for soft woods and 0.13 for steel.

\* Reprinted from the *Journal of Applied Physics*, Vol. 12, No. 1, pages 12-20, January 1941.

The analytical solutions of problems involving heat transfer through solids are based on solutions of the Fourier equation:

$$\frac{dQ}{d\theta} = \rho C \frac{dt}{d\theta} = \frac{\partial}{\partial x} \left( k \frac{\partial t}{\partial x} \right) + \frac{\partial}{\partial y} \left( k \frac{\partial t}{\partial y} \right) + \frac{\partial}{\partial z} \left( k \frac{\partial t}{\partial z} \right),$$

in which  $Q$  is the heat density at the point  $x, y, z$  in Cartesian coördinates. Graphical solutions of this equation for standard shapes such as spheres, cylinders, plates, etc., can be obtained by the use of the Gurney-Lurie<sup>1</sup> charts which involve four dimensionless ratios:

A temperature difference or an unaccomplished temperature change ratio:

$$Y = \frac{T - t}{T - t_1}.$$

A "relative time" ratio:

$$X = \frac{k\theta}{\rho CR^2}.$$

A relative resistance ratio:

$$m = \frac{1}{h} \bigg/ \frac{R}{k} = \frac{k}{hR}.$$

A position ratio:

$$n = r/R,$$

where  $\theta$  = time from start of cooling or heating,  $C$  = specific heat of solid,  $\rho$  = density of solid,  $T$  = constant uniform temperature of surroundings,  $t$  = temperature at position  $n$  within solid at time  $\theta$ ,  $h$  = surface heat transfer coefficient,  $k$  = thermal conductivity,  $r$  = distance from midplane,  $R$  = distance from midplane to surface.

TABLE I  
HEATING TIMES FOR 4-CM SLABS OF VARIOUS MATERIALS

	Time in minutes			
	Heating in gas-free steam		Heating in air	
Temperature change accomplished at center..	50%	99.5%	50%	99.5%
<i>Material</i>				
Commercial copper .....	0.023	0.134	75.5	577
Mild steel .....	0.196	1.16	77.2	589
Loaded rubber compound.....	15.7	93.3	89.5	642
Crude rubber .....	31.4	186.	93.1	650

The relative importance of the surface heat transfer coefficient and the thermal diffusivity is illustrated in Table I which shows the times required to heat large slabs 4 cm thick of several materials under two sets of conditions. In the first case the heating medium is gas-free steam where the surface coefficient is very high, estimated about 0.41 c.g.s. unit. In the second the medium is air at low velocity (approx. 2 m/sec.) with the surface coefficients determined experimentally to be 0.00025 for the metals and 0.00016 for the two grades of rubber. The table shows the times required to change the temperature at the center of the slab



50.0 per cent and 99.5 per cent of the total impressed temperature difference, when the heat is applied uniformly to both surfaces. The effect of changes in the surface heat transfer coefficient on both good and poor conductors is shown by comparing the ratios of the times for 50 per cent temperature change of the metals heated in air and in steam (e.g., about 3300 for copper), with the same ratios for the poor conductors (e.g., about 3 for crude rubber). There is a significant difference in this ratio even for the two metals. The important factor determining the ratio of heating times for slabs of a given thickness is seen to be the ratio of the thermal conductivity of the slab to the surface heat transfer coefficient, which is the parameter " $m$ " above. It should be noticed that the ratio of the 99.5 per cent to the 50 per cent time is almost constant for all materials in a given heat transfer medium, but that it is somewhat greater for slow than for rapid heating.

While the Gurney-Lurie curves have been useful in analyzing some heating and cooling problems, the majority of problems in the rubber industry do not meet the conditions assumed in developing these curves; namely, uniform composition, uniform surface temperature, known and constant heat transfer coefficient, and simple geometric shape. For these and other reasons, it is usually necessary to solve most thermal problems by the actual measurement of the temperature changes in various parts of the sample being studied.

### III. PROCESSING PROBLEMS

Study of the cooling of rubber during mixing operations is of considerable importance, because a large amount of work must be done on the rubber to disperse fine powders uniformly throughout the mass, and the temperature must be kept low enough to prevent "scorching" or prevulcanization. The rapid change of plasticity with temperature<sup>2</sup> for unvulcanized rubber compounds increases the importance of temperature control since the temperature of the rubber determines the magnitude of the shearing forces which break up and disperse the masses of very fine pigment in the rubber.

It is interesting to notice that the process of "warming-up" rubber compounds by a short working of the cold stock on an ordinary two-roll mill, preparatory to further processing such as extruding or calendering, is the only one in which the low thermal conductivity of rubber is an advantage. Since the required heat is generated by internal friction throughout the rubber mass, low conductivity is an advantage rather than a disadvantage since it makes surface cooling effects so small. Heating which would ordinarily require hours by conduction and radiation may be done in five minutes by working the rubber on a mill.

In a typical mill cooling test the average gross power input to the mill-line motor was about 150 hp for a mixing cycle which turned out four 210-lb. batches per hour. After deduction of losses in the transmission system, motor, and mill bearings the net power input was about 121 hp—equivalent to a heat energy rate of 5120 B.t.u./min. The distribution of this energy is shown graphically in Figure 1 in the form of a heat balance diagram. The losses were about 66 per cent to the cooling water as measured by timed water-meter readings and differential multithermocouples, 16 per cent in the form of sensible heat in the rubber in excess of the initial heat in the materials of the batch, as measured by a needle thermocouple, and, by difference, 18 per cent in radiation, convection, and unaccounted-for losses. The total power input would have been sufficient to raise the temperature of the batch to nearly 1000° F, if that were possible without decomposing the rubber.

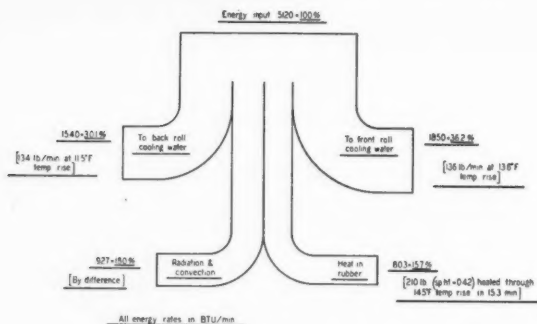


FIG. 1.—Heat balance for a rubber mixing mill.

#### IV. CURING PROBLEMS

The process of vulcanization, in common with many other slow physico-chemical reactions, has a high temperature coefficient. The rate of vulcanization doubles for each rise of about 10 centigrade degrees<sup>3</sup>. This rate of increase varies with the composition of the mixture and with the choice of accelerators; and, particularly in the case of modern delayed-action accelerators, may vary considerably with temperature and time. However, for preliminary analysis it is convenient to make use of this approximate relation between temperature and rate of vulcanization. Variable temperature cures are sometimes evaluated on a more exact basis after determining by test the temperature coefficient of vulcanization for the particular rubber compound—using *T*-50 tests<sup>4</sup>, combined sulfur analysis, modulus, or other criteria of the degree of vulcanization obtained through a range of times at various temperatures.

Typical time-temperature relations for the ends and center of a long sheet of a "pure gum" rubber compound wrapped with thin wet cloth liner on an open metal drum and vulcanized in water are given in Figure 2. Because of the thickness of the wrapped assembly, about 1", it was necessary in this experimental cure to combine several methods for reducing the variation in total vulcanizing effect along the sheet. A long slow "rise" (*A*) was used instead of a suddenly impressed maximum temperature. This was followed by a 15-minute "hold" at 285° F (*B*). At the proper time the heater was blown down by rapid release of pressure to equalize center and surface temperatures (*C*). This reduction of pressure permits removal of heat from the rubber by evaporation of part of the water in the wet interlining cloth, so that at the end of about 2 minutes the whole mass has attained a temperature of 280° F corresponding to the vapor pressure existing in the heater at that time (about 40 psi gauge). The cure was then continued at constant pressure and temperature for an additional period of 20 minutes from the beginning of the "blowdown" (*D*). Controlled slow, rather than rapid, final cooling was employed for 20 minutes (*E*) and the retention of heat in the inner plies was assured by maintaining a constant total pressure of air and steam during the cooling period to prevent evaporation and consequent cooling of the water in the wet liner. At the end of this cooling period the heater was finally blown down rapidly to atmospheric pressure (*F*) and the corresponding temperature (210° F).

Temperatures as determined by the use of waterproof thermocouple equipment in this cure are shown in the figure on two different bases of comparison. At

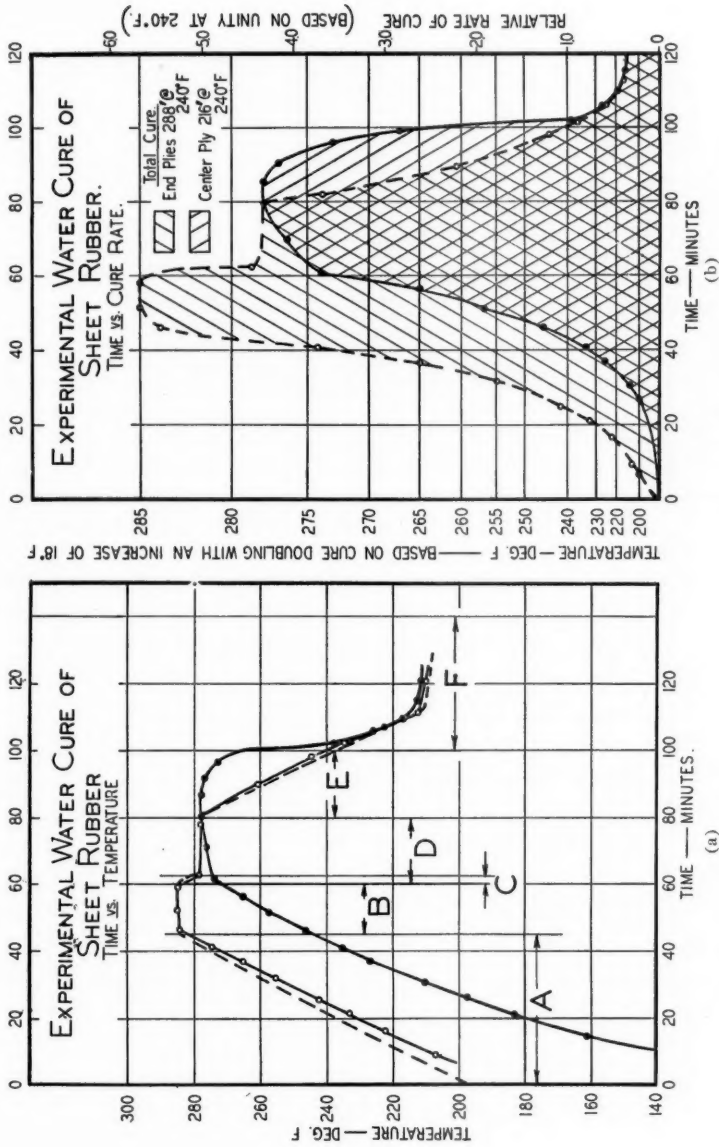


Fig. 2.—(a) Time-temperature relations in water cure of sheet rubber. (b) Time-vulcanization rate relations for cure of Fig. 2(a). Areas under curves represent total vulcanization effects.

the left, in Fig. 2(a), is shown the normal time-temperature relation, while 2(b) shows the relation between vulcanization rate and time, using for convenience a special temperature scale based on the assumed doubling of rate of vulcanization in each 18° F interval. Since degree of vulcanization = vulcanizing rate  $\times$  time, areas under the curves in 2(b) are proportional to total amount of vulcanization. It may be seen that, while the total equivalent effect for the ends of the sheet was that which might be attained in 288 minutes at 240° F, the total for the center was 216 minutes at 240° F, or 75 per cent as much. The variation in this unusually long sheet would, of course, have been much greater had more ordinary methods of vulcanization been employed. For instance, the total equivalent vulcanization for the center ply was increased 17 per cent by the use of the special pressure cooling technique over that which would have been obtained with ordinary "blowdown" cooling.

The enormous advantage in time saving to be gained by application of heat to both sides of a thick rubber article may be illustrated by the comparison of an internal heat cure of a large pneumatic truck tire with another cure of the same tire with no internal heat. The internal heat cure was pioneered in this country by the B. F. Goodrich Company with the advent of the cord tire about twenty years ago. It is based on an initial application of saturated steam at about 340° F and 100 psi gauge to the thick-walled rubber water bag which expands against the interior surface of the tire, followed by a much longer holding period during which the bag temperature is held nearly constant by hot water under sufficient pressure to force into the cord structure some of the surrounding rubber and to knit the whole mass together into the form imposed by the external mold. Proper choice of times and temperatures avoids the necessity of circulation of the hot water used in the main part of the cure, although water is circulated in special cases. External heat is applied according to a pre-arranged schedule of time and temperature starting at a definite time after the initiation of internal heat.

A typical tire cross section with associated water bag and curing mold is shown in Figure 3. On the tire section are shown the locations of the thermocouples used to secure the curves in Figures 4 and 5, which present a comparison of an air bag cure without internal heating and a water bag cure as described above.

The wide difference in uniformity of vulcanization obtained by the two processes is evident. Only by the use in different parts of the tire of compounds curing at four or more different rates could the air bag cure produce results approaching the uniformity obtained in the water bag cure. The difference in vulcanization by these methods is naturally much less in thinner tires such as those used in passenger-car service.

Surface heat transfer rates in open steam and most mold cures are so high in comparison with the low thermal diffusivity of rubber compounds that they may be considered to be infinite. For that reason time-temperature relations in many objects of simple form can be predicted with considerable accuracy. There are, however, some other vulcanization processes in which the heat transfer rates are neither high nor uniform. In these, air, steam-air mixtures of changing composition, or water may be used as the heat transfer medium for a variety of reasons.

Typical time-temperature relations for a portion of an air pressure cure of footwear are shown in Figure 6. Here the initial air temperature of about 210° F was increased during the one-hour rise portion to 250° F and then held

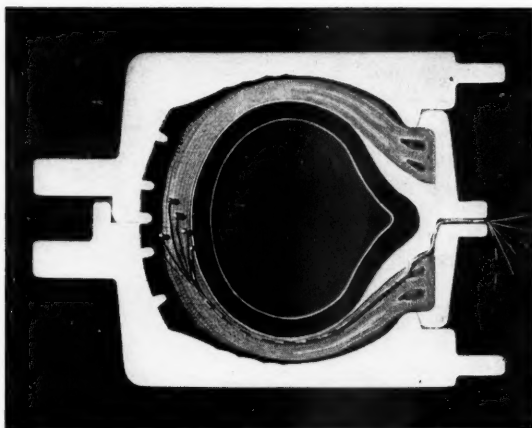


FIG. 3.—Cross section of tire and water bag in steel mold showing locations of thermocouples.

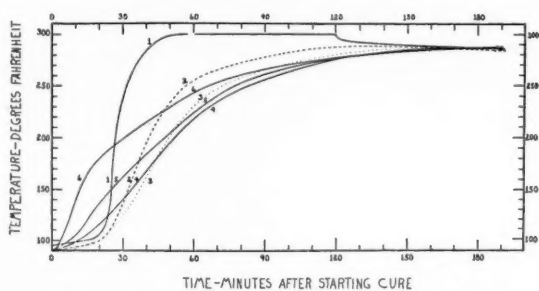


FIG. 4.—Temperatures in a tire during an "internal heat" cure, heat being supplied from both sides. Couples are located as follows: No. 1, at surface of tread next to mold; No. 2, at base of tread; No. 3, at top of 12th ply; No. 4, at top of 8th ply; No. 5, at top of 4th ply; No. 6, at surface of inner (1st) ply next to water bag.

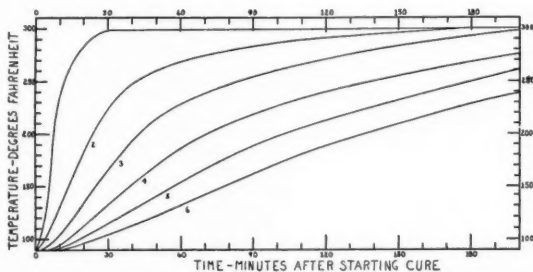


FIG. 5.—Temperatures in a tire during an "air bag" cure, heat being applied from outside only. Couple locations, bag and mold are same as for Fig. 4.

at that temperature for  $1\frac{1}{2}$  hours. Pressure was 30 psi gauge during the first two hours and atmospheric thereafter. The pressure serves to make the rubber-fabric structure of the shoes more compact and to increase the surface heat transfer rate. Radiation and forced convection were chiefly responsible for transfer of heat to the goods. Air temperatures at two representative points in a vulcanizer holding about 4000 pairs of shoes, and the temperature of parts of two typical shoes, are shown. The test from which these data were taken was one of several which indicated that uniformity of convection and radiation heating were the most important factors in obtaining uniform vulcanization throughout the vulcanizer. It was proved that measurement of temperatures in the goods was unnecessary if enough air thermocouples were employed to give a complete picture of the distribution of heat in time and space. This study is typical of many which are not amenable to theoretical analysis.

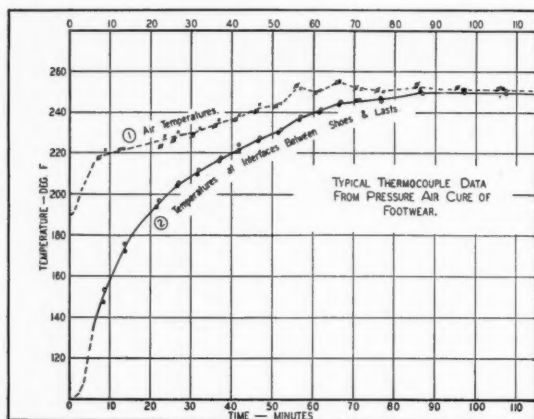


FIG. 6.—Thermocouple data from pressure air cure of footwear.

## V. PRODUCT PROBLEMS

Many rubber products, particularly those built up of rubber and fabric, are subject in service to rapid cyclic stresses with the inevitable conversion of some of the energy input into sensible heat. One of the most important problems of the designer and compounder is that of reducing the amount of heat generated by hysteresis to the lowest value economically practical, and of designing for the best possible dissipation of that unavoidably produced. Continuous high speed operation of modern, heavy-duty motor vehicles under severe road and temperature conditions has made the reduction of temperature due to internal losses in tires one of the most important single problems in tire design.

The measurement of tire temperatures under road and laboratory test conditions is an important aid to the tire designer in evaluating the effects of changes in compounds and constructions. So far as is known, no method of measuring temperatures accurately in a moving tire has ever been put into common practice. The rise in air pressure in a tire from cold to running conditions has been used as a crude gas thermometer measurement of average temperature but this method is subject to serious errors because of thermal expansion and plastic growth in the tire structure, and diffusion of air through the wall of the



inner tube. Moreover, knowledge of an approximate average temperature is not nearly so important as knowing with considerable exactness the temperature and location of the hottest part of the tire. Measurements of this type have been made with fine wire thermocouples inserted with a tool to accurately known depths in selected parts of a tire which has just been stopped. After observing temperatures over a period of several minutes at known time intervals beyond the instant of stopping the tire, the observer may calculate by extrapolation the maximum, under operating conditions, at the point occupied by the thermojunction. Such measurements show maximum internal temperatures in large tires run at high speeds with normal load and inflation pressure to be over 210° F, approaching vulcanization temperatures. Yet the truck or bus owner knows that such tires will render well over 1000 hours of uninterrupted service at speeds of 20 to 60 miles per hour or more.

The thickness of a tire structure must be made as small as practical design will permit unless the tire is to be used exclusively in low speed service. Each increment of thickness not only adds resistance to the flow of heat from all inner layers, raising their temperatures, but it makes its own contribution to the heat which must be dissipated from the surface. Thus the maximum temperature in a tire structure increases very rapidly with increasing thickness. In a number of cases the service of thinner, apparently weaker, tires has exceeded that of standard heavy gauge tires in high speed service because the running temperatures of the thinner tires were lower.

In many applications of V-belts, their life is determined to a considerable degree by their internal operating temperature. The conditions in one acceptance test for V-belts were so severe that some belts failed in a few minutes through heat blowout, literally through pyrolysis of the organic materials in the rubber compounds, and charring of the cotton. Belts of that particular construction were nevertheless known to last several years in ordinary service. Concentrated attack on the problems of compounding and construction finally produced a belt of the same size which ran sufficiently cooler to have a life of 64 hours under the same test conditions, an increase in life of about a thousand-fold.

The extreme temperatures which may be developed in rubber products subject to cyclic stress are illustrated also by the occurrence of heat blowouts in solid tires when they were in common use on motor trucks. Breakdown of the rubber at the thermal center of the tire section, resulting from temperatures of over 500° F, caused the generation of gases under sufficient pressure to burst the overlying layers of rubber. Thermal failures of another type were observed in experimental work on a hydraulic device which used rubber-covered parts as valves to control cold water at high pressure. A jet of high pressure water,  $\frac{1}{4}$ " in diameter, impinging on a layer of rubber,  $\frac{1}{4}$ " thick, which was bonded to metal, produced heat blowouts in the rubber. These failures occurred in a few minutes even when the sample was immersed in water at 40° F under a jet at the same temperature.

Heat transfer problems are of importance occasionally in the design of rubber-lined chemical-processing equipment. The temperatures of reaction vessels may be controlled by means of water jackets or by coils. These heat-transfer surfaces may be covered with rubber for protection against chemical attack. In a typical case of this character a water solution at 160° F in a rubber-lined reaction vessel was to be cooled by means of a surrounding water jacket. Rubber  $\frac{1}{4}$ " thick, having a conductivity of 1.2 B.t.u./(hr.)(ft.)<sup>2</sup>(°F/in.), was to be used to

line the vessel. The cooling water had a mean temperature of 80° F. The circulation conditions inside and outside the tank indicated that the heat transfer coefficient at either wetted surface was about 300 B.t.u./ (hr.) (ft.)<sup>2</sup> (°F). The vessel walls were made of  $\frac{1}{4}$ " thick steel.

The total thermal resistance,  $R$ , of such a wall will be equal to the sum of the resistances of the two water films, the rubber, and the steel: or

$$R = 1/h_s + 1/k_r/t_r + 1/k_s/t_s + 1/h_s,$$

in which  $h_s$  = surface heat transfer coefficient,  $k_r$  = thermal conductivity of rubber,  $t_r$  = thickness of rubber,  $k_s$  = thermal conductivity of steel, and  $t_s$  = thickness of steel.

$$\begin{aligned} R &= 1/300 + 1/1.2/\frac{1}{8} + 1/312/\frac{1}{4} + 1/300 \\ &= 0.003 + 0.104 + 0.0008 + 0.003 \\ &= 0.1108 \text{ [ (B.t.u.) / (hr.) (ft.)}^2 \text{ (°F) ]}^{-1} \end{aligned}$$

or the over-all heat transfer coefficient =  $1/0.1108 = 9.0$  B.t.u./ (hr.) (ft.)<sup>2</sup> (°F).

Thus, it may be seen that the thermal resistance of the  $\frac{1}{8}$ " thickness of rubber is about 95 per cent of the total. The thermal resistance of the water films is negligible in comparison. This is not true, of course, in the case of a bare metal reaction vessel where the water films would have offered approximately 88 per cent of the total resistance. However, it is unfair to compare rubber-lined with bare metal equipment of the same metal composition and thickness. In many cases no metal would serve the purpose, and in most cases any special chemical-resistant alloy would be much thicker and would have a considerably lower thermal conductivity than the thin steel normally used for rubber-lined chemical vessels.

## VI. THERMOCOUPLE AND OTHER HEAT MEASUREMENTS

A discussion of the thermocouple technique used in the rubber industry is necessarily beyond the scope of this paper. A few examples of the type of equipment and circuits used are, however, mentioned to illustrate general design features. Figure 7 shows a typical circuit in a 40-point thermocouple set of iron-constantan wire designed for use in an air heater 8 ft. in diameter x 40 ft. long in which footwear is vulcanized. Note that each circuit is made up of one pair of thermocouple wires continuous from hot junction to cold junction and that switching is done only in the copper leads between cold junctions and potentiometer binding posts in order to eliminate thermoelectric effects in the switch.

Because of the necessity for accommodating testing technique to the tempo of factory operations, the thermocouples are installed in the cars of footwear before they are rolled into the heater. Four cables, each containing ten circuits made up of leads, cold junctions and a packing gland adapter, are arranged for convenient insertion through a single air-tight packing in the heater wall. Connection between cold junctions and leads is made by means of multicircuit connectors. Readings are taken manually at the rate of about 10 per minute with a portable potentiometer. This equipment illustrates the semicommercial adaptation of well-known laboratory methods. The design is based on two main requirements: (a) elimination of all possible thermoelectric effects in spite of severe temperature gradients inside and out of the heater and considerable heat radiation on lead wires and instruments; (b) speed of operation required by the necessity of making test heats as nearly like production heats as possible and

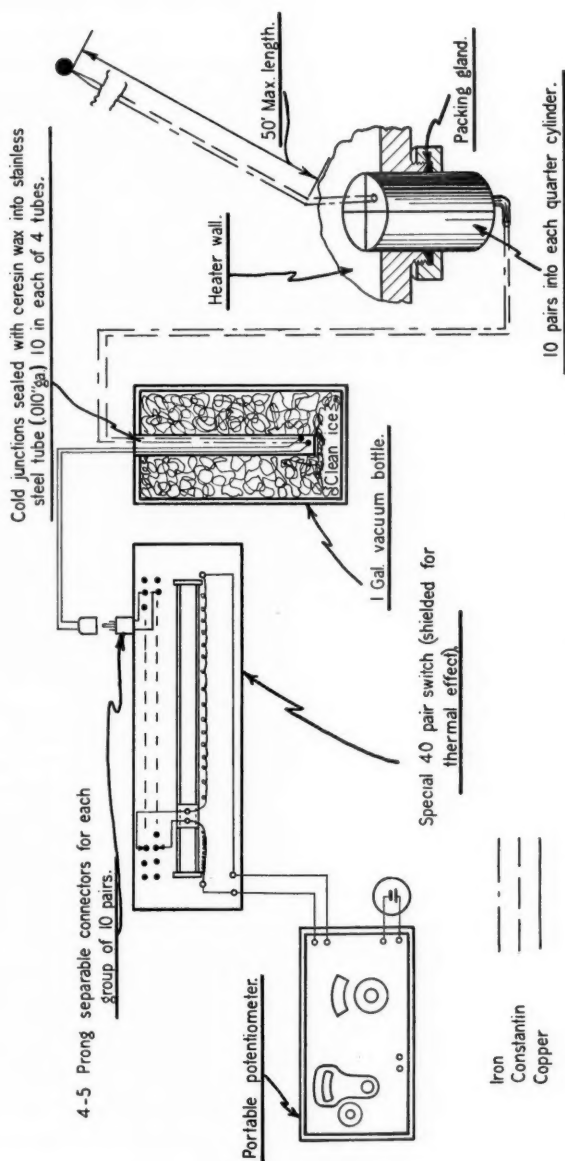


FIG. 7.—Typical circuit in thermocouple set for testing air vulcanizers.

by the fact that frequent readings at each of a large number of points had to be obtained in order to study rapidly fluctuating air temperatures. The curves of Figure 6 are representative of data taken with this equipment.

The importance of avoiding thermoelectric errors in low voltage thermocouple circuits cannot be overemphasized. Thermocouple equipment subject to many such sources of error sometimes is found in otherwise well regulated laboratories. Casual drafts and stray heat radiation often have been observed to cause errors of as much as 0.15 mv in circuits designed to measure about 300° F maximum (about 8 mv). In low range thermoelectric equipment, it is always best to avoid all discontinuities in the thermocouple wires, even though connections are soldered. Automatic or manually controlled cold junction compensators are to be avoided unless the temperature at the cold junction can be measured accurately and prevented from drifting rapidly so that a voltage differential between the two sides of the circuit may be set up. Carefully made cold junctions in clean ice kept in pint or quart vacuum bottles are recommended. Commercially available portable equipment can be relied upon to give results accurate to better than  $\pm 0.5^\circ$  F if it is used carefully and all sources of thermal and calibration error are avoided. The rubber industry as a whole is possibly the largest user of equipment of this type in ranges up to 400° F.

The remarks about compensators do not apply to the several excellent commercial automatic potentiometer type temperature recorders which have built-in cold junction compensators of the nickel resistance-bridge or other type. Instruments of this kind, although usually installed permanently for recording or controlling operations, may sometimes be found suitable for test work. Usually, however, they are not adapted to rapid recording of more than two points and cannot be set up conveniently and quickly enough.

Some use is made of direct-reading thermocouple pyrometers, especially in the measurement of temperatures of mill and calender rolls and of crude and compounded rubber. In measurements of the former type the hot junction is formed at the center of a band of the thermocouple alloys, which is held in sliding contact under light pressure against the moving metal surface of the roll by a hand-held frame. Rubber stock temperatures are read by using a separate hand-held thermocouple which is protected by a small stainless steel hypodermic needle. The direct reading instrument is a sensitive microammeter equipped with a bi-metallic cold junction compensator. These instruments must be carefully checked for calibration errors, transient thermal effects and balance errors. However, the convenience of the hand-held, direct-reading instrument often outweighs its somewhat limited accuracy.

## VII. SUMMARY

The threefold heat problems of the industry are, in order of their occurrence: (1) Controlled removal of heat generated in processing crude rubber. (2) Regulation of heating and cooling processes to give the most nearly uniform vulcanization in the shortest possible time. (3) Measurement and reduction of heat generation in products subject in service to cyclic stress conditions.

Each of the three types of problems engages the attention of chemists and engineers as well as physicists. The chemist is constantly searching for new ingredients and combinations of materials which will promote rapid vulcanization at curing temperatures, that is, 240 to 320° F. The same rubber compounds, when unvulcanized, must be relatively insensitive to processing temperatures up to

about 220° F; when vulcanized they must withstand prolonged use at temperatures above 200° F. The engineer must design curing equipment and related automatic controls. He also must design the combinations of rubber compounds and structural elements which make up the products of the industry. The physicist must measure and analyze the thermal properties of the raw materials, the rubber compounds and the finished products. He also must apply the methods of the physics laboratory to the study in the factory of thermal problems connected with production operations. The cooperation of all is essential in producing for the consumer better products at lower cost.

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# THE EVALUATION OF RECLAIMED RUBBER \*

ROGER A. HUBLIN

## DEVELOPMENT OF THE RECLAIMING INDUSTRY

During the first five years the consumption of reclaimed rubber has increased noticeably. This increase is the result chiefly of the progressive increase in the price of natural rubber, an increase which has induced the rubber industry to use constantly greater quantities of various substitutes in an effort to make the increase in the cost of finished products less than it would be otherwise. On the other hand, in countries whose political economy functions in closed cycles, the use of various substitutes, in conjunction with the growing use of synthetic rubberlike products, in place of rubber has been developed to a considerable degree.

Processes for manufacturing reclaimed rubber have undergone, or are on the point of undergoing, important changes. In addition to the classic alkali process, which still remains the most important commercial process, new processes have been perfected, among the most widely used of which may be mentioned processes with superheated steam and with saturated steam at high pressure, developed in Germany, the Bemelmans process, and the Heyman and Codina process.

Among these new processes, some are based on ideas which have already been the object of numerous more or less fruitful experimentation. They owe their present success in great part to technical improvements in the mixtures employed, improvements which have made it possible to reclaim scrap rubber which could not have been reclaimed twenty years ago by simpler methods. Factories are now equipped with facilities for reclaiming their own waste rubber, or scrap rubber when it can be purchased economically. The majority of these new installations are not constructed to use the alkali process, but to utilize simpler processes, such as those cited above.

## NECESSITY OF A METHOD FOR THE EVALUATION OF RECLAIMED RUBBER

These general developments, which are evidenced by the appearance in the market of a large number of new types of reclaimed rubber, make the problem of the evaluation of reclaimed rubbers of real importance.

It is very important for the rubber technologist to choose, from the various products offered, those which are most suitable to his needs. It is at least just as important that this choice be made strictly on a basis of price.

In the case of those manufacturers who make their own reclaimed rubber, it is likewise highly important to know whether such a change in operation, which necessitates a certain immobilization of capital, will be profitable, *i. e.*, whether it will have a sufficiently favorable effect on the cost of the product for a rapid amortization of the expense involved to be expected.

All these questions lead ultimately to the question: what is the cost of a rubber mixture, containing a particular reclaimed rubber, which meets specifications of quality known in advance?

\* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 16, No. 8, pages 301-306, October 1939; No. 9, pages 329-335, November 1939.



In the following discussion, the possibility of answering this question in a general way will be examined; in other words, can a method be found with which it is possible, by simple means, to determine the relation between the cost and quality of a reclaimed rubber which is to be tested?

#### A REVIEW OF EARLIER WORK

Up to the past few years, there have been few facts which could be correlated in any way and thus make it possible to develop a general method for the evaluation of reclaimed rubber.

Aside from chemical analysis, the classic error is to vulcanize a reclaimed rubber, which has been submitted for examination, with a certain percentage of sulfur, and then to measure the mechanical properties of the vulcanizate. The difficulty in interpreting the results of such tests and the errors which may be involved have been discussed by Winkelmann<sup>1</sup>, by Stafford<sup>2</sup>, and by Palmer<sup>3</sup>. On the other hand, this type of test is, according to Miller<sup>4</sup>, of great practical utility in making an accurate determination of the specific gravity of a reclaimed rubber. The first published work dealing with this question in a general way appeared in 1925, under the authorship of Holt and Wormeley<sup>5</sup>. These authors were interested chiefly in the influence of the resistance to abrasion of a vulcanizate, of the tire-tread type, of the substitution of new rubber by reclaimed rubber. Holt and Wormeley came to the conclusion that, under the conditions of their experiments, the introduction of reclaimed rubber, even in moderate proportions, lowers greatly the resistance to abrasion.

The conclusions and the technique employed in carrying out the tests have been discussed by Bierer and Davis<sup>6</sup>. These authors approached the question from the point of view that substitution of new rubber by reclaimed rubber must be made in such a way that a constant proportion of rubber and fillers is maintained. By following the rules established by these authors, it can be proved that introduction of a small proportion of reclaimed rubber does not impair the resistance to abrasion of a rubber mixture. In addition, Bierer and Davis studied the artificial aging of rubber mixtures containing reclaimed rubber, and found that such mixtures sometimes have excellent aging properties.

In a work devoted to reclaiming rubber, Bary<sup>7</sup> has given examples of an arithmetic method of formulating mixtures containing reclaimed rubber, a method based on the composition of the base recipe. This method does not take into account the cost factor.

Miller<sup>4</sup> has described a series of tests which can be applied to reclaimed rubber, and which are in substance a general method of analysis of reclaimed rubber, including mixing, extrusion properties, plasticity, capacity for absorbing compounding ingredients, physical tests of type mixtures, etc.

In addition to these works, which are concerned directly with the evaluation of reclaimed rubber, numerous investigations have been described which deal with the influence of the addition of reclaimed rubber to rubber mixtures on the properties of the latter. Changes in tensile strength, elongation, modulus of elasticity, and mechanical properties in general, have been the object of experiments by Shepard<sup>8</sup>, Dawson<sup>10, 13</sup>, Vogt<sup>11</sup>, Sanderson<sup>15</sup> and Miller<sup>14</sup>. The experiments of Vogt and of Sanderson are of particular interest, for here substitution was made with due regard to the compositions of the base mixtures.

The influence of reclaimed rubber on hardness was studied by Dawson<sup>10, 13</sup> and by Williams<sup>16</sup>. The permanent set and elasticity, both static and dynamic, of mixtures containing reclaimed rubber were measured by Dawson<sup>10, 13</sup> and by

Vogt<sup>11</sup>. Resistance to abrasion was studied thoroughly by Holt and Wormeley<sup>5</sup> and by Bierer and Davis<sup>6</sup> in connection with investigations on the value of reclaimed rubber in general. Sanderson<sup>15</sup> and Carpenter and Sargisson<sup>17</sup> studied resistance to tearing. Ingmanson and Gray<sup>18</sup> carried out experiments on compression tests. Fatigue effects were studied by Sanderson<sup>15</sup> and by Cooper<sup>19</sup>.

Natural and artificial aging were given special attention by Dawson<sup>13</sup>. Swelling in solvents was studied by the R. T. Vanderbilt Co. Laboratories<sup>20</sup>. Absorption of water by mixtures containing reclaimed rubber was investigated in particular by Cooper and Daynes<sup>21</sup> and by Soule<sup>22</sup>. Finally the use of reclaimed rubber was the subject of a special publication of the R. T. Vanderbilt Co. Laboratories<sup>23</sup>.

Nevertheless, neither in these latter works nor in the preceding ones have the authors attempted to work out practical rules for the evaluation of reclaimed rubber on a basis of price, the essential factor involved. Merely a comparison of one or more physical properties has been the primary object. From the industrial point of view, such a comparison has only a relative value, and before a choice of reclaimed rubbers can be made, it is absolutely necessary to take into account the question of price.

By comparing critically the results of the investigations cited above and of further work by the present author, it has been attempted in the present paper to develop a method which, with the aid of a relatively small number of tests, makes possible a complete comparison of the relative costs and properties of various mixtures adaptable to a particular service.

#### OBJECT AND FIELD OF APPLICATION OF THE METHOD OF EVALUATION

As has been mentioned above, the essential object of methods of evaluation of reclaimed rubbers is the rapid and accurate determination of the cost of a reclaimed-rubber mixture, formulated for a particular service.

Conversely, if it is specified that a rubber mixture must not exceed a definite cost, it should be possible to decide whether any such mixture can be formulated with ordinary compounding ingredients. Furthermore, it should then be possible to follow the changes in the cost of a mixture with changes in the price of a reclaimed rubber, with changes in the rubber market, etc.; in brief, it should be possible to solve all problems which arise in connection with the use of reclaimed rubber.

#### THE BASIC PRINCIPLES

To solve any of these problems in a quantitative way, the first and indispensable condition is obviously that the particular problem itself be presented in quantitative terms and in as precise a form as possible.

First of all it is necessary to know the use to which the mixture is to be put. A comparison of several reclaimed rubbers is of definite significance only when the service conditions are clearly defined. For example, a reclaimed rubber which gives excellent results in rubber soles is not necessarily of value in the manufacture of industrial products. The service can be specified either by defining the use directly, *e.g.*, pneumatic tires, flooring, inner tubes, etc. or by a set of definite specifications. Each particular service involves certain requirements, such as color, resistance to abrasion, flexibility, etc., which immediately set a limitation to the choice of materials which can be used; *e.g.*, it is impossible to take advantage of the relatively excellent quality of black reclaimed rubbers in the production of red inner tubes.

The method of manufacture should then be defined in all its details. Here a second set of limitations is encountered, most of which are concerned with the properties of the particular mixture before vulcanization, including its behavior in extrusion, its moulding properties, its vulcanizing properties, its plasticity, its adhesive properties, etc. In general, an examination of the results obtained makes it possible to fix numerical limits to all these measurable properties, and thus to assure satisfactory processing.

In the third place, the characteristics of a finished article should be clearly defined insofar as these characteristics are essential to the particular service. If the service is of the ordinary kind, and is not defined by specifications, a series of properties established by service conditions can be chosen by comparison with the properties of products which have been satisfactory under ordinary service conditions of the particular article. If there is a specification with definite numerical requirements, two cases present themselves: (1) the properties specified are defined in ordinary terms, *e.g.*, hardness, specific gravity, tensile strength, resistance to abrasion, etc., and (2) the use of practical tests. In the latter case, it is still necessary to interpret these requirements in ordinary terms of hardness, tensile strength, etc.

Actually this procedure is usually followed, whatever the conditions, in choosing ordinary formulas.

Among the properties on which it is absolutely necessary to obtain quantitative measurements or a series of measurements by this means are hardness (measured by the Shore Durometer or ball apparatus), tensile properties (preferably in the form of stress-strain curves), and other important properties, the choice of which depends on the service contemplated, *e.g.*, resistance to abrasion, aging, swelling in solvents, etc.

Reclaimed rubbers which are to be tested and compared should be examined in a preliminary way, with a view to being able to write recipes with adequate knowledge of their properties. Reclaimed rubbers should be analyzed chemically in the usual way, and tested according to the general scheme. In particular the following properties should be determined quantitatively:

- (1) Inorganic substances and fillers
- (2) Nature of the fillers
- (3) Acetone extract
- (4) Total sulfur
- (5) Free sulfur
- (6) Rubber hydrocarbon
- (7) Specific gravity

Very satisfactory procedures have been described for all these determinations, and attention will be called, in passing, only to the very practical method of C. O. Weber for determining the filler content, which is based on solution in  $\alpha$ -nitronaphthalene, and which has been used with much success in analyzing reclaimed rubbers.

Specific gravity or density<sup>4</sup> is determined by vulcanizing a mixture of 95 parts of reclaimed rubber and 5 parts of sulfur, and measuring the density of the product. The density of the reclaimed rubber itself is derived from the formula:

$$d = \frac{100A}{105 - 2.41A}$$

where  $d$  is the density of the reclaimed rubber, and  $A$  is the density of the vulcanized mixture.

The price of the reclaimed rubber should of course be known with exactitude. If the reclaimed rubber is produced in the same factory, an accurate determination of its cost is not always the simplest part of the problem. However, a discussion of this determination is beyond the scope of the present work.

#### EXPERIMENTAL LAWS OF SUBSTITUTION

The method of evaluation of reclaimed rubbers which is proposed in the present work is based on a number of experimental laws on the relations between the properties of simple mixtures in which new rubber is replaced progressively by reclaimed rubber.

To be able to apply these laws to the present problem, it is necessary to comply, in these substitutions, with certain rules.

(1) After having chosen a type of formula which conforms to the intended service of the particular article, and which contains only new rubber, the latter is replaced by its equivalent of reclaimed rubber, taking into account the composition of the reclaimed rubber. If, for example, the percentage of new rubber is reduced from 100 to 50, the 50 parts of new rubber removed are replaced by a proportion of reclaimed rubber corresponding to 50 parts of rubber hydrocarbon in the reclaimed rubber.

(2) The necessary adjustments are made, in accordance with the nature and percentage of the fillers, to retain the same general composition of the recipe, taking into account the chemical composition of the reclaimed rubber.

Up to this point, there is nothing particularly new. The rules of rational substitution have already been worked out by Bierer and Davis<sup>6</sup>, by Sanderson<sup>12</sup> and by Bary<sup>7</sup>.

(3) It must then be decided what properties of the mixtures derived from the base mixture containing only new rubber are to be maintained identical to those of the base new-rubber mixture and the mixtures containing reclaimed rubber, and an effort must then be made to keep these properties constant by adjusting such ingredients as the percentages of fillers and plasticizing agents. It is also possible to maintain the same time of vulcanization for the reclaimed rubber mixtures as for the base mixture, as this can be done merely by making the necessary adjustments in the percentages of sulfur and accelerator. Likewise, by controlling the nature and percentage of plasticizing agents, it is possible to obtain mixtures having nearly the same plasticities.

(4) A series of properties should be chosen as a means of following any changes which result from the substitutions. Such a series might include, for example, tensile strength, elongation at rupture, resistance to abrasion, resistance to tearing, etc.

(5) Finally it is necessary to adjust the total volume of fillers to maintain the hardness constant in the complete series of mixtures derived from the base mixture. This last condition is of great importance for the validity of the laws of substitution. It should be added that this does not necessarily mean that the volume of each of the fillers must be kept constant. If the conditions which have just been described are satisfied, the physical properties of mixtures prepared by substitution of reclaimed rubber for new rubber in the base mixture are related in certain very simple ways. These relations can be shown to advantage in graphical form in an analogous way to the graphic method which has been used in studying the properties of alloys or mixtures of salts; *i.e.*, Konovloff diagrams.

Assume that two mixtures, of the following limiting compositions:

- (1) Mixture A containing only new rubber
- (2) Mixture B containing only reclaimed rubber,

have been formulated, and as already mentioned, these mixtures have been so designed that they have the same hardness, and contain the same ingredients, with the necessary adjustments. Let their compositions be expressed on the basis of 100 parts of new rubber or reclaimed rubber. According to the principles discussed above, each mixture derived from mixture A by partial replacement of new rubber with reclaimed rubber can be regarded as composed of a blend of mixture A and the complementary proportion of mixture B. If the weight of

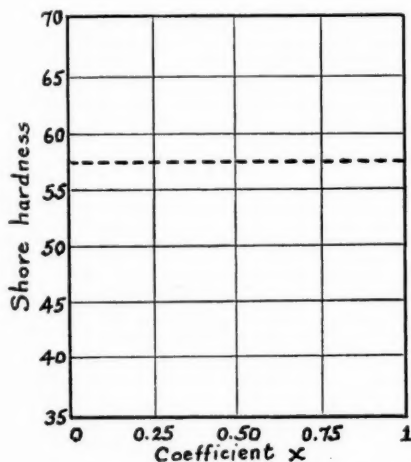


FIG. 1.—Constancy of the hardness of a continuous series.

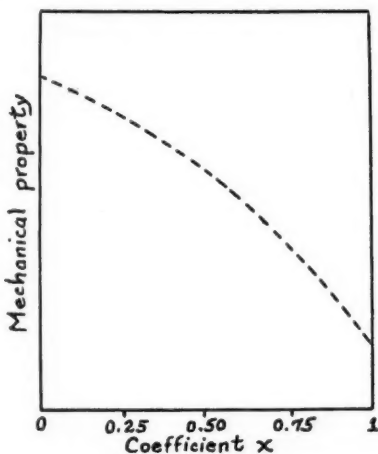


FIG. 2.—Continuity in the change of a characteristic physical property. Completely convex curve.

new rubber replaced by reclaimed rubber is  $x$ , the weight of any ingredient in this mixture can be represented by the equation:

$$M_x = xM_B + M_A(1 - x)$$

where  $M_x$ ,  $M_A$  and  $M_B$  represent the weights of ingredient M in the respective formulas, based on 100 parts of rubber hydrocarbon, in mixture X and in the base mixtures A and B, respectively.

Accordingly  $x$  represents, not only the proportion of new rubber replaced by reclaimed rubber, but also the apportionment coefficient. It is particularly convenient to use  $x$  as a variable to represent the compositions of mixtures intermediate between mixture A and mixture B. To represent the change in any property of these mixtures as a function of the proportion of reclaimed rubber, a graph is constructed with the  $x$  values as the abscissa and the  $y$  values of the particular property as the ordinate. The graph obtained in this way is analogous to the eutectic diagrams of alloys or to the boiling-point curves of mixtures of liquids.

When this very convenient method of representation is utilized, the experi-

mental laws relating the properties of such a series of mixtures can be defined as follows:

- (1) The hardnesses of mixtures of a series are identical, and are equal to the hardness of the extreme mixtures (see Figure 1);
- (2) The changes in mechanical properties are continuous, without abnormalities, retrocessions, etc.;
- (3) The curves showing these changes have no maxima or minima;
- (4) The directions of curvature of these curves do not change; *i. e.*, each curve is either convex throughout (see Figure 2) or concave throughout (see Figure 3), and has no points of inflection;
- (5) The radius of curvature is generally great throughout the entire length of the curve;

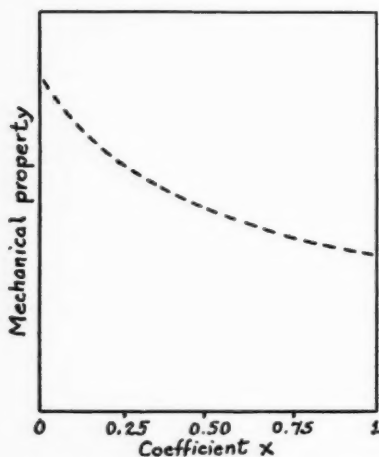


FIG. 3.—Continuity in the change of a characteristic property. Completely concave curve.

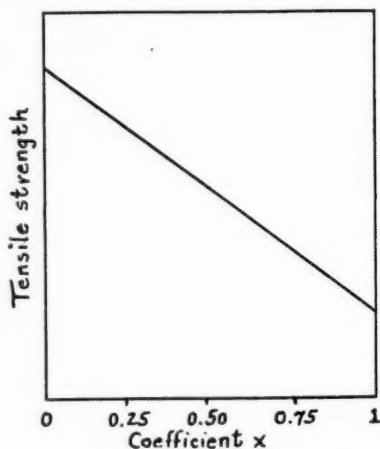


FIG. 4.—Linear change in tensile strength.

(6) In the case of tensile strength, the function is approximately a linear one (see Figure 4);

(7) The forms of the stress-strain curves are similar for all the mixtures of a series. These curves practically coincide up to elongations of 50 per cent of the elongation at rupture, and the differences are relatively small, even at higher elongations (see Figure 5).

In summary, these several principles prove that the law of mixtures applies with good approximation to mixtures intermediate between the limiting mixtures, provided the hardness is maintained the same in all cases.

#### VERIFICATION OF THE LAWS OF SUBSTITUTION

To illustrate this perhaps uninteresting conclusion, it seems advisable, even at the expense of being irksome, to show a few examples drawn from the literature and from experiments by the present author.

*Tests by Sanderson*<sup>12</sup>.—The reclaimed rubber tested by Sanderson was an alkali-process whole pneumatic-tire reclaimed rubber, containing approximately



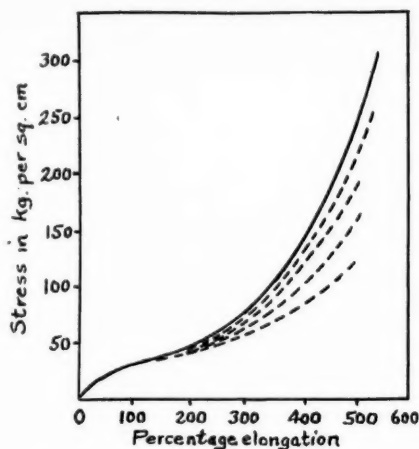


FIG. 5.—Stress-strain curves of a continuous series.

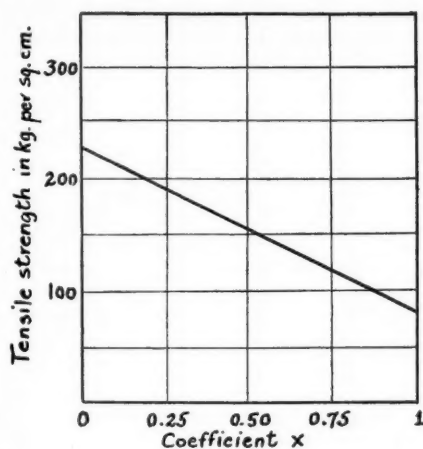


FIG. 6.—Data obtained by Sanderson.

55 per cent of rubber hydrocarbon. The mixtures containing this reclaimed rubber were vulcanized for 60 minutes at 126.4° C (see Table I).

The measurements in Table I are shown graphically in Figure 6. It is evident that, with the exception of one of the mixtures, the linear relation between tensile strength and  $x$  is very satisfactory.

TABLE I

Rubber .....	100	90	80	75	50	25	—
Whole-tire reclaim .....	—	18.2	36.4	45.5	91	136.5	182
Sulfur .....	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Carbon black .....	49.2	47.2	45.2	44.2	39.2	34.2	29.2
Clay .....	11.6	10.4	9.25	8.67	5.78	2.89	—
Litharge .....	0.6	0.2	0.1	0.1	—	—	—
Whiting .....	7.46	6.71	5.97	5.60	3.73	1.87	—
Zinc oxide .....	16.4	14.7	13.1	12.3	8.2	4.1	—
Stearic acid .....	4	4	4	4	4	4	4
Mineral rubber .....	10.5	9.45	8.4	7.88	5.25	2.63	—
Pine tar .....	10.5	9.45	8.4	7.88	5.25	2.63	—
Mercaptobenzothiazole .....	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Apportionment coefficient.....	0	0.1	0.2	0.25	0.5	0.75	1
Tensile strength (kg. per sq. cm.).....	226	230	190	180	150	118	84
Elongation at rupture (percentage) .....	590	560	520	515	470	485	325

*Comparison of reclaimed rubbers made by the alkali process and by the superheated-steam process.*—In this series of tests, two series of mixtures derived from the same base mixture by replacement of new rubber were compared:

(1) a series containing reclaimed rubber made from pneumatic-tire peelings by the alkali process;

(2) a series containing reclaimed rubber, also made from pneumatic-tire peelings, but by the superheated-steam process.

The rubber hydrocarbon content of the alkali-process reclaimed rubber was approximately 58 per cent; that of the superheated steam-process reclaimed

rubber was approximately 57 per cent. The mixtures were vulcanized 20 minutes at 140° C (see Table II).

In this series of mixtures, the Shore hardness was kept constant within 1 point, an approximation which, from a practical point of view, is quite satisfactory.

TABLE II

## MECHANICAL PROPERTIES

(Tests obtained with Schopper rings)

Smoked sheet .....	100	75	75	50	50	25	25	5	5
Zinc oxide .....	5	5	5	5	5	5	5	5	5
Sulfur .....	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Vulkacit thiuram .....	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Vulkacit D.M. ....	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Stearic acid .....	1	1	1	1	1	1	1	1	1
Reclaimed rubber No. 1.	—	43	—	86	—	129	—	165	—
Reclaimed rubber No. 2.	—	—	44	—	88	—	132	—	167
Whiting .....	80	62	61	44	42	26	23	10	8
Apportionment coefficient	0	0.25	0.25	0.5	0.5	0.75	0.75	0.95	0.95
Shore hardness .....	58	58	59	59	58	59	58	59	59
Tensile strength (kg. per sq. cm.) .....	200	152	161	117	126	78	91	42	62
Elongation (percentage) ..	500	425	430	360	345	340	330	260	260
Resistance to abrasion (cc. per kw.-hr. by Williams machine) ....	800	940	870	1220	1060	1750	1450	2250	1930
Resistance to tearing (kg. per cm., Heathcote method) .....	90	50	56	32	42	19	27	7	19

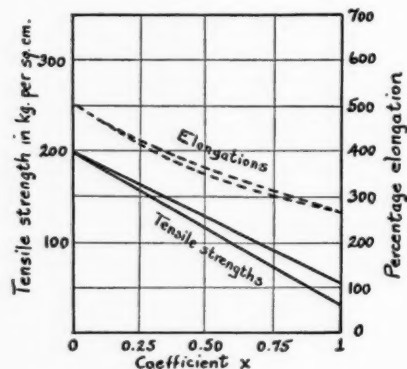


FIG. 7.—Comparison of reclaimed rubbers (Table II).

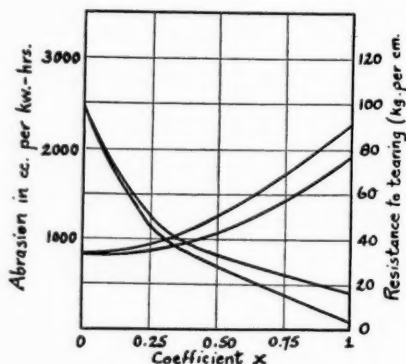


FIG. 8.—Comparison of reclaimed rubbers (Table II).

The measurements obtained with this series are shown graphically in Figures 7 and 8.

An examination of these measurements shows that, in all the cases studied, the laws of substitution as outlined above are confirmed experimentally with an approximation which can be regarded as excellent.

## PRINCIPLE OF THE METHOD OF EVALUATION

With the aid of these experimental laws, it is possible to develop a general method of evaluation and comparison of reclaimed rubber.

First of all, let it be assumed that the basic conditions, defined at the beginning of this discussion, of the laws of substitution are fulfilled, and that the same method of graphic representation is to be adopted. In principle, the method consists essentially in relating the graphic representation of the important mechanical properties to a simple graphic representation of the costs of the mixtures involved. With this representation as a basis, it is easy to establish the relations between the mechanical properties and the costs of the mixtures in any series under investigation. In each case, the cost which should be chosen for these comparisons is, obviously, the cost of a unit volume, *e.g.*, cost of a cubic decimeter.

It can be readily demonstrated (see notes I and II) that, when the formula is based on 100 parts of rubber hydrocarbon, the total volume of ingredients in any mixture of a series is, between the volumes of the limiting mixtures, a linear function of the apportionment coefficient  $x$ . Likewise the total cost of the ingredients in a mixture varies linearly in the range between the total costs of the limiting mixtures (note III).

The cost per unit volume can, therefore, be expressed as the quotient of the two linear functions of  $x$  (see note III).

Therefore, to obtain a complete graphic representation from which the cost of any mixture of predetermined quality, *i.e.*, the increase in cost for the particular property in question, can be calculated, all that is necessary is to trace, on the same system of coördinates, straight lines representing the changes in volume and in cost of all the ingredients, and their experimental curves representing the changes in the physical properties concerned (see Figure 9). Five scales are readily constructed for practical needs as follows:

- Two vertical scales for 2 different physical properties;
- Two vertical scales for the cost and volume, respectively;
- One horizontal scale for the apportionment coefficient.

There is nothing to prevent extending this graphic representation to various other physical properties; in this case all that is necessary is to construct their curves on tracing paper on the same scale as that of the apportionment coefficient, and to bring them into coincidence with the cost graph by transparency. By means of this graphical method, curves representing physical properties as a function of cost can be readily constructed.

## NOTE I—SYMBOLIZATION OF MIXTURES

Let  $A_1, A_2, A_3, \dots, A_i, \dots$ , represent the different ingredients which make up the composition of a given mixture. Let  $m_1, m_2, m_3, \dots, m_i, \dots$  be the weights of ingredients  $A_1, A_2, A_3, \dots, A_i, \dots$ , comprising the formula of this mixture. Its composition is then:

$$[m_1A_1, m_2A_2, m_3A_3, \dots, m_iA_i, \dots]$$

Let  $A_1$  be new rubber,  $A_2$  be reclaimed rubber, and

$$m_1 + \alpha m_2 = 100$$

where  $\alpha$  is the rubber hydrocarbon content of the reclaimed rubber. This symbolization applies to the type of formula in which the total weight of rubber is maintained equal to 100.

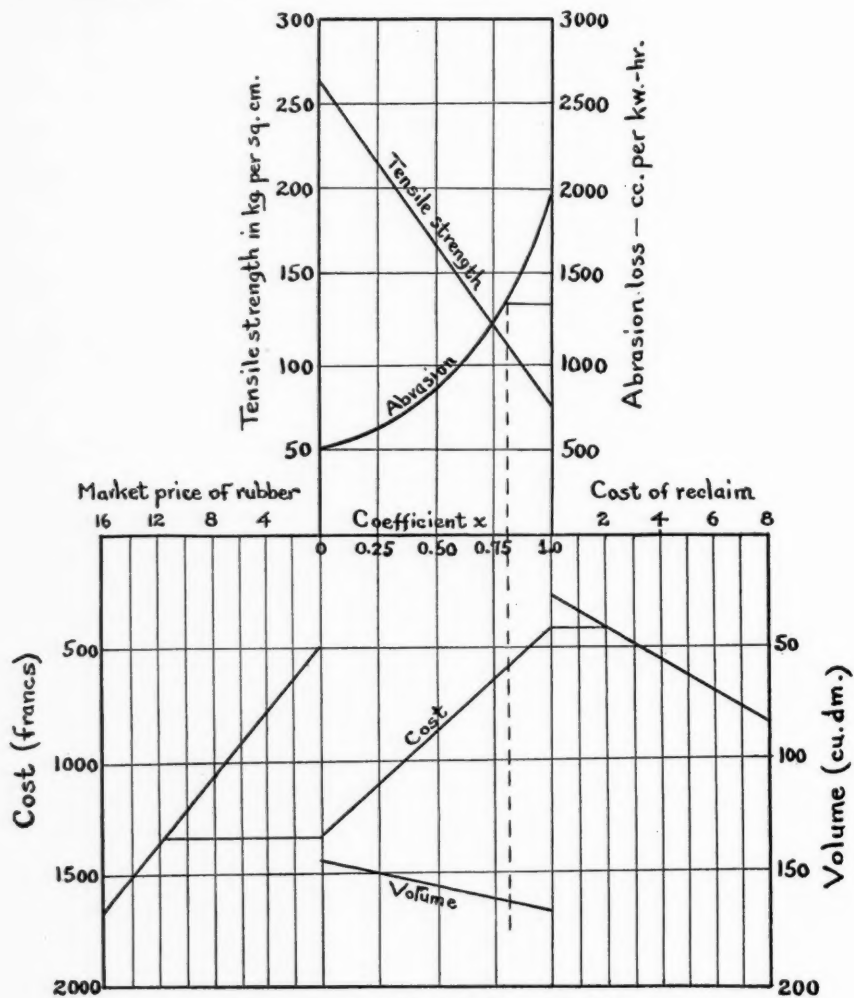


FIG. 9.—General method of graphic representation.

The total weight of the mixture is:

$$M = \sum_{i=0}^{i=n} m_i$$

If  $v_i$  is the volume of ingredient  $A_i$ , the total volume of the mixture is:

$$V = \sum_{i=0}^{2=n} v_i$$

The density  $d$  of such a mixture is:

$$d = \frac{\sum m_i}{\sum v_i}$$

Let  $p_i$  be the cost of a unit weight of ingredient  $A_i$ ; then the total cost of the ingredients comprising the mixture is:

$$C = \sum p_i m_i$$

The cost of a unit volume of this mixture is then:

$$\frac{C}{V} = \frac{\sum p_i m_i}{\sum v_i}$$

In a series of mixtures in which substitution is carried out in accordance with the rules already outlined, the mixture having the partition coefficient  $x$  can be symbolized as follows:

The mixture

$$[m_1^x A_1, m_2^x A_2, m_3^x A_3, \dots m_i^x A_i \dots]$$

has for its total weight:

$$M^x = \sum m_i^x$$

for its total volume:

$$V^x = \sum v_i^x$$

for its density:

$$d^x = \frac{\sum m_i^x}{\sum v_i^x}$$

for its total cost:

$$C^x = \sum p_i m_i^x$$

and for its cost per unit volume:

$$\frac{C^x}{V^x} = \frac{\sum p_i m_i^x}{\sum v_i^x}$$

In a system of mixtures in which two substitutions have been made, the following symbolization is applicable in the same way:

$$[m_1^{xy} A_1, m_2^{xy} A_2, m_3^{xy} A_3, \dots m_i^{xy} A_i \dots]$$

$$M^{xy} = \sum m_i^{xy}$$

$$C^{xy} = \sum p_i m_i^{xy}$$

$$V^{xy} = \sum v_i^{xy}$$

$$d^{xy} = \frac{\sum m_i^{xy}}{\sum v_i^{xy}}$$

$$\frac{C^{xy}}{V^{xy}} = \frac{\sum p_i m_i^{xy}}{\sum v_i^{xy}}$$

It is possible to generalize further, and to consider a number  $n$  of any transformations whatever:

$$[m_1^{(xy)n} A_1, m_2^{(xy)n} A_2, m_3^{(xy)n} A_3, \dots]$$

To obtain the expressions for the new system, it is necessary only to transform, identically to the method used for  $m_1$ , the exponents of  $M$ ,  $V$ ,  $d$ ,  $C$ , and  $C/V$ .

*Note.*—In this method of representation, the exponents do not have their usual meaning of powers, but are only identification symbols like those used in tensor notation.

#### NOTE II—CALCULATION OF THE TOTAL VOLUME

By definition:

$$V^x = \sum v_i^x$$

Now:

$$v_i^x = \frac{m_i^x}{d_i}$$

if  $d_i$  is the true density of the mixture  $A_1$ .

But also, by definition of the substitution of coefficient  $x$ :

$$m_i^x = x m_i^1 + (1-x) m_i^0$$

Hence:

$$v_i^x = \frac{x m_i^1}{d_i} + (1-x) \frac{m_i^0}{d_i}$$

If

$$\frac{m_i^1}{d_i} = v_i^1 \text{ and } \frac{m_i^0}{d_i} = v_i^0$$

then

$$v_i^x = x v_i^1 + (1-x) v_i^0 \quad (1)$$

$V^x$  can then be calculated:

$$\begin{aligned} V^x &= \sum v_i^x = \sum (x v_i^1 + (1-x) v_i^0) \\ &= \sum x v_i^1 + \sum (1-x) v_i^0 \\ &= x \sum v_i^1 + (1-x) \sum v_i^0 \end{aligned}$$

However, in consequence of Equation (1):

$$\sum v_i^1 = V^1$$

$$\sum v_i^0 = V^0$$

Hence:

$$V^x = x V^1 + (1-x) V^0$$

#### NOTE III—CALCULATION OF THE TOTAL COST OF UNIT VOLUME

$$C^x = \sum p_i m_i^x$$

$$C^x = \sum p_i (x m_i^1 + (1-x) m_i^0)$$

which can be written:

$$C^x = \sum p_i x m_i^1 + \sum p_i (1-x) m_i^0$$

or:

$$C^x = \sum p_i m_i^1 + (1-x) \sum p_i m_i^0$$

or again:

$$C^x = x C^1 + (1-x) C^0$$

From this expression for  $C^x$ , an expression for  $C^x/V^x$  can be derived:

$$\frac{C^x}{V^x} = \frac{x C^1 + (1-x) C^0}{x V^1 + (1-x) V^0}$$



In general:

$$\frac{C^1}{V^1} = \frac{C^0}{V^0}$$

It follows that the functional relation of  $C^x/V^x$  to  $x$  is not in general a linear one, a fact of considerable significance. On the contrary,  $C^x/V^x$  is the quotient of two linear functions of  $x$ , and therefore can be used directly for graphical calculations.

It should be noted that, in the diagram represented by Figure 9, the upper part, which represents the physical properties as functions of  $x$ , can be worked out once and for all for the particular series of mixtures in question, provided a satisfactory constancy of the properties of the ingredients and of the processing operations is assumed. This is also true of the straight line of the total volumes. On the contrary, the costs of the mixtures vary as a function of the state of the market.

It will next be shown that there is available a very interesting method for studying the effects of variations in the prices of raw materials. As a matter of fact, over a period of several months, the greatest variations in the prices of raw materials are most frequently those of crude rubber and reclaimed rubber. If, then, it is assumed that the costs of the other ingredients are fixed, the cost of mixture A ( $x = 0$ ) obviously depends only on the rubber market, and is a linear function of the market price. Likewise the cost of mixture B ( $x = 1$ ) depends only on the prices of reclaimed rubbers, and is a linear function of the price of this material.

The preceding graphic representation (Figure 9) can be completed by a simply constructed graph which gives, as a function of the market prices of these materials, the total cost of the sum of the ingredients of mixtures A and B, *i.e.*, the position of the extreme positions of the straight line representing the prices.

There is then available a very complete system with which it is possible to calculate very easily the effects of variations in the market price of crude rubber or of reclaimed rubber on the price of a mixture which has some invariable physical property.

In general the price of reclaimed rubber remains constant for long periods, and therefore it is possible to limit the diagram to variations only in the price of rubber.

#### EXAMPLES TO SHOW THE APPLICATION OF THE METHOD

The method which has been described can, for example, be utilized for studying a mixture designed for the cover of coal conveyor belts. Experience has shown that excellent service in this respect can be expected of a mixture with the following properties:

- Hardness (Shore): 60
- Tensile strength: 150 kg. per sq. cm.
- Elongation at rupture: 500 per cent
- Resistance to abrasion (du Pont machine): 1200 cc. per kw.-hr.

In addition to this, successful processing of the unvulcanized mixture requires:

- Time of vulcanization: less than 15 min. at 140° C.
- Plasticity (Williams at 70° C, 2 cc. sample, 5 kg. weight, 5 min. compression): 5 min. max.

An example can now be shown, in which two different reclaimed rubbers are used:

(1) *Reclaimed rubber A*, made from automobile tire treads by the alkali process; rubber hydrocarbon content approximately 55 per cent; price 3 fr. 50 per kg.

(2) *Reclaimed rubber B*, made from whole tires by the alkali process; rubber hydrocarbon content approximately 45 per cent; price 2 fr. 25 per kg.

The general method can be applied to this problem. First of all, a formula containing only new rubber and meeting all the requirements cited above is written, with the help of practical experience. Formula No. 1 in Table III conforms fully to all the conditions specified. Following methodically the general method, formula No. 5 for reclaimed rubber A, and formula No. 9 for reclaimed rubber B are derived. In these formulas the following adjustments were made:

(1) The percentages of sulfur and accelerator to meet the required time of vulcanization;

(2) The volume of fillers to satisfy the hardness requirement;

(3) The percentages of plasticizing agents to maintain the necessary degree of plasticity.

In this way the preliminary requirements are fulfilled. The intermediate formulas Nos. 2, 3 and 4, corresponding to  $x$  values of 0.25, 0.50 and 0.75 for series A, and 0.25, 0.50 and 0.75 for series B, can then be written.

The hardness, plasticity and time-of-vulcanization values are within the limits set for all these mixtures, the extreme mixtures Nos. 1, 5 and 9 satisfying themselves. It remains therefore to study experimentally the tensile strength, elongation and abrasion values to obtain a complete picture of the two series.

The results of these tests are included in Table III. To these are added data on:

$C_x$  = the total cost of all the ingredients.

$V_x$  = the total volume of all the ingredients for the limiting mixtures 1, 5, and 9.

The values determined in this way are plotted on the general diagram, and the corresponding curves and lines are drawn (see Figures 10 and 11). It then becomes possible to determine for what values of  $x$  the tensile strength, elongation and resistance-to-abrasion requirements are fulfilled simultaneously. These values are found to be:

0.61 for reclaimed rubber A

0.50 for reclaimed rubber B

Continuing with the graphic method, it is possible to determine quickly, from the particular  $x$  value, the corresponding  $C^{xy}$  value for each mixture. It will be found that:

$$\frac{C^x}{V^x} = 7.53 \text{ for reclaimed rubber A}$$

$$\frac{C^x}{V^x} = 7.97 \text{ for reclaimed rubber B}$$

The use of reclaimed rubber A is therefore the more favorable choice to obtain the properties desired for the service. There is no difficulty in writing the formula of the resulting mixture.

TABLE III

## MIXTURES FOR CONVEYOR BELTS

Series	1	2	3	4	5	6	7	8	9
No. of mixture.....	100	75	50	25	—	75	50	25	—
Smoked sheet .....	—	45.25	95.0	135.75	181	—	—	—	—
Reclaimed rubber No. 1.	—	—	—	—	—	55.5	111	166.5	222
Reclaimed rubber No. 2.	—	—	—	—	—	—	—	—	—
Sulfur .....	2.7	2.6	2.5	2.4	2.3	2.55	2.40	2.25	2.1
Mercaptobenzothiazole ..	0.3	0.28	0.26	0.24	0.22	0.275	0.250	0.225	0.2
Tetramethylthiuram disulfide .....	0.3	0.28	0.26	0.24	0.22	0.275	0.250	0.225	0.2
Phenyl- $\beta$ - naphthylamine .....	1	1	1	1	1	1	1	1	1
Stearic acid .....	3	2.5	2	1.5	1	2.5	2	1.5	1
Pine tar .....	3	2.75	2.5	2.25	2	2.7	2.3	1.9	1.5
Mineral rubber .....	4	3	2	1	—	3	2	1	—
Zinc oxide .....	5	4.5	4	3.5	3	4.5	4	3.5	3
Carbon black (Micronex)	45	36	28	20	12	35	25	15	5
Total weight .....	164.3				202.70				236.0
Apportionment coefficient	0	0.25	0.50	0.75	1	0.25	0.50	0.75	1
Optimum time of vulcani- zation (min. at 140° C).	15	14	14	13	12	14	14	13	12
Hardness (Shore) .....	65	—	—	—	65	—	—	—	65
Plasticity (Williams)....	4.3	—	—	—	4.5	—	—	—	4.4
Tensile strength (kg. per sq. cm.).....	280	235	196	136	110	236	174	128	75
Elongation at break (percentage) .....	675	650	610	550	440	640	600	520	420
Resistance to abrasion (cc. per kw.-hr.).....	800	940	1100	1400	2000	980	1200	1740	2800
C <sub>x</sub> (francs) .....	1838	—	—	—	768	—	—	—	595
d <sub>x</sub> .....	1190	—	—	—	1320	—	—	—	1450
V <sub>x</sub> (cu. dm.).....	144	—	—	—	154	—	—	—	163

## COMPARISONS OF RECLAIMED RUBBERS

The method under discussion can be utilized in a general way for comparisons of reclaimed rubbers. It is necessary only to choose arbitrarily some particular type of mixture, and to apply to it the general method, choosing as a criterion of quality a property which can be easily measured, such as tensile strength. It is of advantage to choose a mixture of medium hardness (65-70 by a Shore instrument) and containing an inert filler, because differences in quality between different reclaimed rubbers are most in evidence under these conditions.

Experiments have shown that under these conditions:

(1) The relative values of different reclaimed rubbers obtained by the use of a mixture of a certain hardness are, in general, still true when a mixture of different hardness is used.

(2) The relative values of different reclaimed rubbers which are being compared are in general, not altered by a change in the type of the filler.

(3) The relative values of different reclaimed rubbers, judged by tensile strength, remain in general, the same when another criterion, such as resistance to abrasion or resistance to tearing, is used as a basis of comparison.

In these three general rules, only relative values are referred to, and no mention is made of the proportions of crude rubber and reclaimed rubber, for these are subject to change.

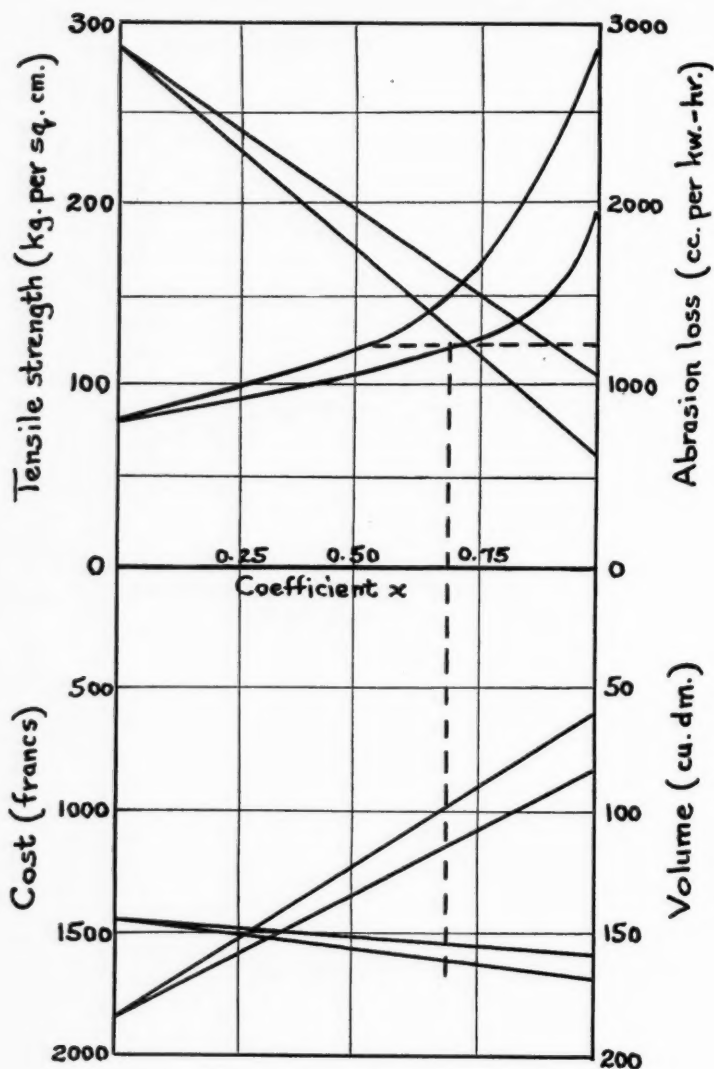


FIG. 10.—Example of the quantitative application of the graphic method.

An immediate application of this method is in studying modifications of reclaiming processes. In general, changes in the process of manufacturing reclaimed rubber involve two consequent changes:

- (1) A change in the intrinsic quality of the reclaimed rubber;
- (2) A change in the cost of the reclaimed rubber.

In this case it is sufficient to apply the method of comparison defined in the present work to different products, obtained by changing the operating conditions, in order to decide on the particular method of manufacture which

gives, not a reclaimed rubber of the lowest cost, but a rubber-reclaim mixture of a minimum cost, with physical properties better than the minimum properties chosen beforehand.

Likewise an economical choice of different commercial reclaimed rubbers can be made by means of the method under discussion. It should be added that, in conformity to the principle described for writing the limiting mixtures of a series, *i.e.*, the two mixtures which contain only reclaimed rubber and only crude rubber, respectively, it is necessary first of all to make all adjustments to take care of the special properties of the reclaimed rubber (correct percentage of sulfur, accelerators, etc.) so that a comparison can then be made of mixtures in which each reclaimed rubber is used in such a way as to conform to its peculiar characteristics.

The method can likewise be used with success in the control testing of shipments of reclaimed rubber. In this case all that part of the method which involves costs is disregarded, and only the relation between the coefficient  $x$  and the physical properties is used as a basis of comparison. The constancy of these relations should be maintained within satisfactory limits. Such a method of control is much more precise than an examination of the properties of a single type of reclaimed-rubber mixture. As a matter of fact, in this latter case the experimental errors are considerable, whereas curves of physical properties can be constructed with a satisfactory degree of approximation because of the multiplicity of the tests.

#### GENERALIZATION OF THE METHOD

The method of comparison which has been described can be regarded as a means of studying the saving which can be made by the use of reclaimed rubber in rubber mixtures. There are, of course, other ways of lowering the cost of rubber mixtures, *e.g.*, cheap diluents such as "mineral rubber", factice, and plasticizing agents, which in general are cheaper than the rubber mixture itself, can be added. Then again, advantage can be taken of various types of fillers to replace the relatively expensive carbon black or zinc oxide.

In many cases, the question arises as to which means of approach should be chosen. Would it, for example, be more economical, in maintaining a given standard of quality, to use a diluent, *e.g.*, mineral rubber, or to substitute reclaimed rubber for part of the new rubber? This question cannot be answered in any simple way.

However, as will be shown, it is possible to make a rational choice by making use of a more general method of comparison, derived from the restricted method which has been described in the present work.

Rather than unnecessarily extend the present paper, it seemed best to limit the discussion to a single example—the choice between substitution by reclaimed rubber and dilution by mineral rubber. It is assumed that some particular reclaimed rubber has already been chosen, and that the curve of the physical properties as a function of the apportionment coefficient has already been constructed from experimental data. Experience has shown that, up to proportions of the order of 40 per cent by weight of rubber, the addition of mineral rubber to any mixture in a series does not change the hardness materially, but does impair the physical properties.

To represent the compositions of complex mixtures, derived from mixtures of the preceding series by dilution with mineral rubber, recourse can be had to a system of rectangular coordinates, where the abscissa represents the apportion-

ment coefficient  $x$ , and the ordinate represents the proportion (by weight of the rubber) of mineral rubber  $y$ . The coördinates of any point on the diagram show directly the composition of the corresponding mixture (see Note IV).

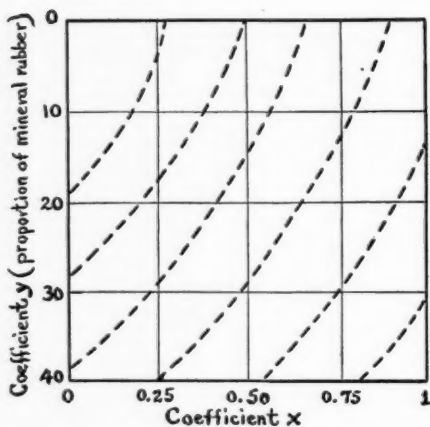


FIG. 11.—System with two variables.

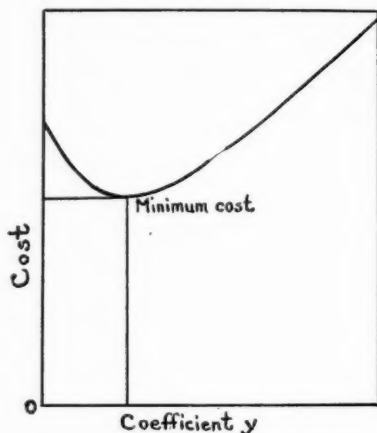


FIG. 12.—Method of determining minimum costs.

#### NOTE IV

According to the symbolization already adopted:

$$m_i^{xy} = xm^{i0} + (1-x)m_i^o.$$

$$R^{xy} = yR^o$$

where  $R^{xy}$  represents the quantity of diluent in the mixture ( $x, y$ ).

To express graphically the changes in the particular physical property under investigation, it is necessary this time to have recourse to a spatial representation, i.e., to a surface. Utilizing the methods of geometry, the lines of intersection of the plane  $xy$  with a series of planes parallel to  $xy$ , the heights of which are progressively greater are projected on this plane  $xy$ . All points on such a line represent the compositions of mixtures having the same particular physical property. It is necessary then only to graduate in cost units the line corresponding to the minimum value of the same physical property to be able to choose the most economical mixture.

In calculating the cost in practice, recourse is had to a diagram derived directly from that used in the restricted method. To the  $x$  axis of this diagram is joined another diagram graduated in costs and volumes, and the straight lines of the cost  $C^{xy}$  are constructed for a certain number of conveniently spaced percentages of mineral rubber.

Likewise a straight line representing volumes for the series  $R=0$  is constructed. To calculate the cost of a mixture  $xy$ ,  $C^{xy}$  on the corresponding straight line, is used, and, for the volume, the value  $Vx + R$ , the density of mineral rubber being very close to 1.

The resulting diagram offers a means of calculating readily the cost of a mixture represented by any point on a line of the same property.

As a ready means of choosing the most economical composition of rubber mixture, a graph showing the relation between cost and proportion of diluent



is constructed from a series of values calculated in this way. The mathematical sign of the variation, and the minima, if there are any, will then be evident (see Figure 12).

We shall limit ourselves to this single example, for the object is only to show that it is possible by means of suitable modifications, to take advantage of the proposed method each time that new rubber is partially replaced by reclaimed rubber, irrespective of any other kind of change.

Methods of a similar kind can be used each time that there are two ways of lowering the cost of a mixture. This is, for example, the case when it is a choice either of substituting reclaimed rubber for new rubber, or of substituting an inert filler for an active filler.

If it is desired to compare still other methods of lowering costs, a series of comparisons must be made one at a time, with two simultaneous substitutions at the most.

#### EXPERIMENTAL APPLICATION

In applying the method experimentally, it is of course advisable to work under well standardized conditions. The particular specifications which are adopted are relatively unimportant, provided they are followed rigidly at all times. The specifications of the American Society for Testing Materials, of the D.I.N., or those of the British Standards Institution can be followed with equal chances of success.

It has already been pointed out that it is necessary, above all else, to adjust the limiting formulas so that they satisfy the conditions of substitution. The corresponding experimental work follows ordinary methods, and the subject need not be discussed in the present paper.

There is, however, one point which deserves attention. It has been shown that, to construct curves or surfaces showing the relations between physical properties and apportionment coefficients, it is necessary to prepare a large number of mixings. There is, however, a simple artifice by which it is possible to simplify this work enormously, and to assure more uniform results than by preparing each mixing separately. As already pointed out, the composition of any intermediate mixture of a series, even in the most complicated cases, can be represented as a linear function of the compositions of the limiting mixtures with the aid of the apportionment coefficients. Accordingly it is sufficient to prepare, under already standardized operating conditions, sufficient quantities of these mixtures, and then to blend them in various proportions, calculated in advance, to form the intermediate mixtures required. Obviously this blending of mixtures must be done methodically, and the portions of the limiting mixtures should be subjected to the same working conditions. For example, in the investigation described in Table III, it is necessary to prepare only three base mixtures 1, 5 and 9, and then to blend two of these at a time to obtain mixtures 2, 3, 4, 6, 7 and 8.

As has already been mentioned, the physical measurements should, as a general rule, be carefully standardized to avoid all errors resulting from varying operating conditions.

In constructing the necessary diagrams, it is possible, in the simple case of comparing reclaimed rubbers, to make on the tracing a type diagram, whose scales are sufficiently long to include most ordinary cases which may be encountered. On this tracing are placed the experimental values for each particular case.

## CONCLUSIONS

Examples have been given to illustrate a method of evaluation of reclaimed rubbers which takes into account the costs of the materials tested. When correctly applied, this method gives a rapid and, at the same time, precise answer to all questions of cost and quality which may arise in connection with the use of reclaimed rubber.

In concluding this discussion, attention should be called to an important point. It has been proved fairly conclusively that, if an effort is made to define in a precise manner any problem to be solved, it is possible to apply rational methods to it. With these methods it is possible to avoid much futile experimentation, and to obtain directly results which are a quite satisfactory approximation to the correct ones. This is true, not only in studying and evaluating reclaimed rubbers, but also of problems in general which arise in connection with compositions and costs of various mixtures. In almost all cases it is possible, by making use of analogous methods of procedure, to save considerable time and effort.

It appears to be certain that, thanks to progress in the technique and standardization of testing, it will be possible to make a truly systematic study of rubber compounding.

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# NEW DEVELOPMENT IN RUBBER RECLAIMING \*

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The history of rubber reclaiming has been given by Alexander<sup>1</sup>, and it is therefore intended only to make a brief reference to the well-known acid and alkali processes, the latter having proved to be by far the most successful method of reclaiming vulcanized rubber.

The alkali process, introduced by Marks<sup>2</sup> in 1899 had the outstanding advantage of simultaneously removing, from the waste, free sulfur, of which from 3 to 5 per cent was present, of destroying the fabric and of plasticizing the waste, this being accomplished by heating in a closed vessel under steam pressure with caustic soda. The acid process destroyed only the fabric, and plasticization by heat was performed in another operation in a separate vessel: by this method little or no free sulfur was removed from the waste. This latter disadvantage has since disappeared, for, with modern rubber compounding, there is little free sulfur left in vulcanized rubber.

In recent years there have been widespread changes in the manufacture of rubber goods, particularly in the case of pneumatic motor tires, which are now the main source of raw material for reclaimed rubber. Organic accelerators, anti-oxidants and carbon black have made vulcanized rubber a very tough, resilient article, extremely resistant to aging and to heat, one of the chief agents used in rubber reclaiming. For example, modern motor tire treads, which are heavily reinforced with carbon black, are not so amenable to alkali and heat treatment, and tire treads reclaimed by this process have finally to be plasticized and made homogeneous by a much longer mechanical milling and refining treatment than was formerly necessary; in spite of this the treads still produce a proportion of rough, unrefinable material which has to be separated and rejected from the final reclaim. This increase in milling time, combined with lower finished production due to rejected unrefinable material, has had the effect of greatly increasing the manufacturing cost of the reclaim. Research was therefore started with the object of evolving a process which would successfully offset these difficulties caused by the changes in the properties and characteristics of the initial waste. The result of this work has been the creation of reclaimed rubber from which the disadvantages mentioned have been largely eliminated.

It has been observed that scrap motor tires that had not undergone any natural aging or other usage were much less amenable to reclaiming by the alkali process than similar waste after normal life. It was thought that the use of anti-oxidants, improved compounding and vulcanizing technique, had very materially decreased the tendency of the tires to pass from the elastic to the plastic state when subjected to the alkali or heat reclaiming process. Research was therefore directed towards inducing increased plasticity, and this was achieved by the application of carefully controlled quantities of oxygen at suitable stages of the heat-reclaiming process. It was found most advantageous to introduce this new process between the alkali and mechanical treatment. This involved disintegrating the dry treated waste to a suitable particle size and subjecting the same

\* Reprinted from *Transactions of the Institution of the Rubber Industry*, vol. 16, No. 5, pages 252-259, February 1941.

to a heat treatment in a closed vessel in the presence of moisture and oxygen. The degree of pasticity is accurately controlled by the temperature, duration of treatment and the amount of oxygen used. Alkali tire-reclaim, which before this treatment was found very difficult to plasticize and refine smoothly, and which produced a proportion of rough, unhomogeneous reclaim, was after this treatment easily massed into a sheet on a mill and, when strained, refined out smoothly into thin sheets and gave only a small quantity of rough, unrefinable material. Waste rubber without canvas, when ground to a fine powder and heated with steam and oxygen and softeners in a closed vessel, produced material which could easily be massed together on a mill and, when strained and refined, gave a smooth reclaim. This process was found so successful in commercial practice that it forms the basis of a British patent<sup>3</sup> and corresponding patents in all important rubber manufacturing countries.

Some doubt existed at first as to the aging properties of reclaims made with oxygen as an agent for assisting depolymerizing and plasticizing of the waste, and exhaustive tests were made in comparison with standard alkali-reclaim. These tests show that treatment by oxygen had no deleterious effects, and that the product so produced was equal in all respects to standard reclaim.

Details of these tests are as follows:

COMPARISON OF PHYSICAL AND CHEMICAL PROPERTIES OF WHOLE-TIRE RECLAIMS  
MADE BY THE STANDARD ALKALI PROCESS AND BY THE ALKALI-OXYGEN PROCESS

A=Whole tire reclaimed by standard alkali process.

B=Whole tire reclaimed by alkali-oxygen process.

Analysis	A	B
Specific gravity .....	1.17	1.17
Ash .....	20.73	20.63
Acetone extract .....	8.82	8.91
Alcoholic-potash extract .....	1.50	1.50
Cellulose .....	1.85	1.75
Carbon content .....	12.00	12.21

It is to be noted that the chemical analyses of the two reclaims are virtually identical, indicating the physical nature of the new process.

*Physical properties*

	A		B	
	Tensile strength (kg. per sq. cm.)	Elongation (per cent)	Tensile strength (kg. per sq. cm.)	Elongation (per cent)
Cure (5 per cent sulfur)				
20 min. at 141° C.....	57	415	59	420
Plastometer test (Williams)	Plasticity	Recovery	Plasticity	Recovery
70° C .....	440	180	372	144

The plasticity tests show that reclaim B is distinctly more plastic than A, whereas the cure test shows practically identical products, indicating that this plasticity difference disappears on curing. This is most satisfactory.

*Aging test* of the following tire carcass mixings, using heptaldehydeaniline (heptene base) as the accelerator:

	A	B
Reclaim A .....	37.50	—
Reclaim B .....	—	37.50
Smoked sheet rubber.....	50.00	50.00
Zinc oxide .....	2.50	2.50
Mineral oil .....	2.00	2.00
BLE antioxidant .....	0.25	0.25
Sulfur .....	2.50	2.50
Heptane Base .....	0.10	0.10

*Physical properties before aging*

Cure	A		B	
	Tensile strength (kg. per sq. cm.)	Elongation (per cent)	Tensile strength (kg. per sq. cm.)	Elongation (per cent)
20 min. at 134° C.....	154	700	159	705
45 min. at 134° C.....	149	670	156	674
60 min. at 134° C.....	168	627	176	645
90 min. at 134° C.....	169	620	174	620

*Physical properties after aging in oxygen-bomb 48 hours at 70° C with an oxygen pressure of 21 kg. per sq. cm.*

20 min. at 134° C.....	117	635	124	673
45 min. at 134° C.....	116	620	120	635
60 min. at 134° C.....	117	590	133	615
90 min. at 134° C.....	97	575	105	575

As with the unmixed cured reclaims, the two carcass test-compounds show similar properties, a slight advantage is indicated in the B compound.

*Aging of lightly-compounded cured reclaims vulcanized in 20 min. at 141° C*

	A	B
Reclaim A .....	1000	—
Reclaim B .....	—	1000
Sulfur .....	20	20
Zinc oxide .....	30	30
Butene accelerator .....	2	2

*Physical properties*

	A		B	
	Tensile strength (kg. per sq. cm.)	Elongation (per cent)	Tensile strength (kg. per sq. cm.)	Elongation (per cent)
Before aging .....	73	420	71	420
After aging for 24 hours in oxygen-bomb at 70° C with an oxygen pressure of 21 kg. per sq. cm.....	44	295	48	318

*Aging of a heel compound*

	A	B
Smoked sheet .....	130.00	130.00
Reclaim A .....	210.00	—
Reclaim B .....	—	210.00
Ground waste .....	210.00	210.00
Carbon black .....	72.00	72.00
Clay .....	8.00	8.00
Litharge .....	8.00	8.00
Zinc oxide .....	35.00	35.00
Stearic acid .....	2.50	2.50
Sulfur .....	11.90	11.90
Safex accelerator .....	3.50	3.50
BLE antioxidant .....	3.00	3.00

*Physical properties before aging*

Cure	A		B	
	Tensile strength (kg. per sq. cm.)	Elongation (per cent)	Tensile strength (kg. per sq. cm.)	Elongation (per cent)
8 min. at 156° C.....	99	336	96	340
12 min. at 156° C.....	95	320	96	340
20 min. at 156° C.....	88	295	88	320

*Physical properties after aging in oxygen-bomb for 48 hours at 70° C with an oxygen pressure of 21 kg. per sq. cm.*

8 min. at 156° C.....	69	235	76	233
12 min. at 156° C.....	67	180	74	210
20 min. at 156° C.....	66	190	65	189

The above tests clearly indicate that alkali-oxygen reclaim B yields as good a finished product as can be obtained by using standard alkali-reclaim A.

It is recognized that many rubber mixes containing large proportions of alkali tire reclaim do not extrude or calender as smoothly as is desired, unless the compounds are heavily loaded with fillers. This is particularly noticeable in shoe mixes, wherein specially smooth sheets are required for embossing. In addition, experience has shown that some tire carcass mixes containing large proportions of alkali tire-reclaim have a tendency to scorch in compounds in which thiazole accelerators are used. Research on this subject has proved that this scorching is partly due to the alkali left in the reclaim; even reclaims containing less than 0.01 per cent of alkali scorch in some compounds. These considerations were borne in mind during the research previously mentioned, and investigations were therefore directed to the possibility of evolving a neutral, non-scorching, whole tire reclaim that would flow smoothly in calendered compounds, extrude well, and be equal in all other respects to ordinary alkali whole-tire reclaim.

It was necessary to devise a process wherein caustic alkalies were not used for the destruction of the cellulose. A chemical was finally selected which, when heated with tire waste in a standard reclaiming vessel, destroyed the cotton fabric, and partially plasticized the waste. After washing and drying, the product was considerably tougher and more difficult to masticate than standard alkali-reclaims in the dried stage. It was unsuitable for finishing. However, after disintegration and treatment with oxygen and heat under pressure, the latent plasticity was enormously increased. On being milled, the product sheeted rapidly, strained without excessive heat, and refined smoothly into thin sheets, leaving practically no unrefinable material. For future reference this material is called reclaim M.

The qualities required of reclaim to confer to compounds maximum ease of calendering and extrusion are not readily expressed as a function of specific scientific tests. It is sufficient to state that such reclaim must be characterized by smoothness of texture, absence of tackiness, and recovery sufficiently low so as not to induce any distortion after extrusion, or creeping in calendering. Compounds containing substantial percentages of reclaim M exhibit these qualities to a superlative degree, even when used in lower-gravity compounds containing only moderate percentages of fillers.

Tests on reclaim M show it to be virtually neutral. The standard test consists of four hours' aqueous boiling and titration of the wash, with bromthymol blue as indicator. The following tests were based on compounds containing thiazole accelerators. No data are available on compounds containing basic accelerators, but it is surmized that, on account of the neutral state of reclaim M, a slight modification of the compound would be necessary to adjust the cure.

On a friction calender, tire-carcass stocks made with reclaim M behave like alkali stocks, but the tendency to scorch is greatly reduced. This has been demonstrated in practical use and in the laboratory scorch test, as later set out. This lessening of the tendency to scorch is of major importance, for not only does it almost eliminate the costly hazard of scorched compounds, but it enables larger percentages of reclaim to be utilized.



COMPARISON OF PHYSICAL AND CHEMICAL PROPERTIES OF WHOLE TIRE RECLAIMS  
MADE BY THE ALKALI-OXYGEN PROCESS AND BY THE NEUTRAL-OXYGEN PROCESS

B=Whole tires reclaimed by alkali-oxygen process

M=Whole tires reclaimed by neutral-oxygen process

*Analysis*

	B	M
Specific gravity .....	1.17	1.17
Ash .....	20.63	15.23
Acetone extract .....	8.91	10.01
Alcoholic-potash extract .....	1.50	1.20
Cellulose .....	1.75	1.91
Carbon content .....	12.21	15.55

It will be noted that the acetone extract is a little higher with reclaim M than with B. This is probably due to the saponifiable influence of alkali on the original scrap. The considerably lower ash content of reclaim M is mainly due to all the tire treads being completely incorporated in the reclaim, leaving practically no unrefinable tailings: this is clearly shown in the carbon determination, which is about 3.25 per cent higher in reclaim M. In addition, alkali treatment always results in an ash increase, due to absorbed alkali.

*Physical properties*

Cure (5 per cent sulfur)	B		M	
	Tensile strength (kg. per sq. cm.)	Elongation (per cent)	Tensile strength (kg. per sq. cm.)	Elongation (per cent)
20 min. at 141° C.....	59	420	45	335
Plastometer test (Williams, at 70° C) .....	Plasticity 372	Recovery 144	Plasticity 460	Recovery 109

The unmixed stocks result in somewhat lower tensile strength and elongation figures for reclaim M. This is characteristic of the process, but the result is of no practical consequence, for the physical properties of compounds containing reclaim M are equal to, or better than, those of compounds using any other type of reclaim. It is now generally conceded that reclaim-sulfur cure tests are of little or no importance for assessment of their ultimate compounding value. The plasticity tests show reclaim M to be distinctly firmer.

*Aging test, using mercaptobenzothiazole as accelerator*

	B	M
Reclaim B .....	37.50	—
Reclaim M .....	—	37.50
Smoked sheet rubber.....	50.00	50.00
Zinc oxide .....	2.50	2.50
Mineral oil .....	1.60	1.60
Laurex (zinc laurate).....	0.40	0.40
BLE antioxidant .....	0.25	0.25
Sulfur .....	2.50	2.50
Mercaptobenzothiazole .....	0.45	0.45

*Physical properties before aging*

Cure	B		M	
	Tensile strength (kg. per sq. cm.)	Elongation (per cent)	Tensile strength (kg. per sq. cm.)	Elongation (per cent)
20 min. at 134° C.....	176	640	174	650
45 min at 134° C.....	186	605	191	595
60 min. at 134° C.....	159	600	169	600
90 min. at 134° C.....	157	560	169	590

*Physical properties after aging in oxygen-bomb for 48 hours at 70° C, with an oxygen pressure of 21 kg. per sq. cm.*

20 min. at 134° C.....	177	595	195	590
45 min. at 134° C.....	185	545	190	545
60 min. at 134° C.....	150	540	159	535
90 min. at 134° C.....	118	520	133	515

In the above test reclaim M shows physical properties slightly superior to those obtained when using reclaim B both before and after aging.

*Scorch test on tire-carcass compound, with mercaptobenzothiazole as accelerator*

The method of comparing the relative scorch tendencies induced by reclaims B and M was based on that described by Buchan<sup>4</sup>. Briefly, it involves progressive heating in boiling water of suitable standard-size pellets cut from the compounds concerned. The plasticity and recovery figures are determined on the Williams plastometer after regular intervals of time, the temperature of plasticity testing being 70° C.

*Compound for scorch tests*

	B	M
Smoked Sheets .....	420.00	420.00
Reclaim B .....	350.00	—
Reclaim M .....	—	350.00
Zinc oxide .....	50.00	50.00
Magnesia .....	6.00	6.00
Stearic acid .....	20.00	20.00
Sulfur .....	26.00	26.00
MBT accelerator .....	3.25	3.25

*Heated in water at 100° C*

Plastometer tests before aging	B		M	
	Plasticity	Recovery	Plasticity	Recovery
	205	Nil	235	Nil
5 min. ....	268	Nil	261	Nil
10 min. ....	267	6	263	Nil
15 min. ....	274	5	265	Nil
20 min. ....	310	6	271	Nil
35 min. ....	446	301	297	Nil
40 min. ....	554	436	300	3
60 min. ....	845	655	467	300
75 min. ....	Cured	Cured	582	444

*Physical properties before aging*

Cure	B		M	
	Tensile strength (kg. per sq. cm.)	Elongation (per cent)	Tensile strength (kg. per sq. cm.)	Elongation (per cent)
30 min. at 134° C.....	168	657	138	690
60 min. at 134° C.....	159	640	167	618
90 min. at 134° C.....	168	603	168	617
150 min. at 134° C.....	147	600	153	587

*Physical properties after aging in Geer oven for 5 days at 80° C*

30 min. at 134° C.....	157	610	191	659
60 min. at 134° C.....	149	572	153	520
90 min. at 134° C.....	119	530	123	500
150 min. at 134° C.....	100	450	93	429

This test indicates clearly that the compound containing reclaim M has considerably less tendency to scorch than that containing reclaim B whereas, apart from

the somewhat slower start of cure of compound M, the vulcanizates are reasonably identical in physical properties, both before and after oven-aging. The advantage of reclaim M in freedom from scorching has been proved by means of practical tests on a large scale. This result is not really surprising, for all alkali reclaims contain distinct quantities of adsorbed alkali, such as can be removed only by prolonged aqueous extraction, which is quite impossible in commercial practice. Mercaptobenzo-thiazole and many other accelerators of the thiazole type are considerably activated by alkalies and, in consequence, it is reasonable to expect that reclaim completely free from alkalies, when used with such accelerators, would exhibit less tendency to scorch.

The author wishes to express his appreciation for the assistance given in preparing this paper by W. J. Leonard, W. E. Stafford and R. A. Wright, members of the technical staff of the Rubber Regenerating Co., Ltd., and to this Company for the facilities provided by them.

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# STUDIES OF SYNTHETIC RUBBER. III

## INFLUENCE OF IRRADIATION WITH ULTRAVIOLET LIGHT ON THE DEGREE OF POLYMERIZATION AND STRUCTURAL VISCOSITY OF VARIOUS SYNTHETIC RUBBERS \*

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The structural viscosity of a colloidal solution is formulated by the de Waele-Ostwald equation:

$$\log \eta = \log K + (1-n) \log P \quad (1)$$

Dogadkin and Pewsner<sup>1</sup> reported on the structural viscosities of natural rubber solutions and the influence of irradiation of ultraviolet light on them. The influence of irradiation on the structural viscosities of various synthetic rubbers is very important, and it is interesting to discuss their internal structures. Therefore the present author measured the relative viscosities ( $\eta$ ) of various synthetic rubber solutions under various pressures. The synthetic rubbers included Neoprene, Oppanol-B 200, Oppanol-C, Buna-S and Perbunan, pale crepe rubber being added to compare with these synthetic rubbers.

The Waele-Ostwald equation can be modified as follows:

$$\log \eta = \log K' - n' \log P/P_0 \quad (2)$$

where  $P$  is the total pressure applied to the liquid which flows out into the capillary tube of the viscometer, and  $P_0$  the pressure due to the weight of the liquid itself. When no excessive pressure is applied to make the liquid flow in the capillary tube,  $P$  is equal to  $P_0$ . Then, Equation (2) can be simplified as follows:

$$\log \eta = \log K'$$

Arrhenius and Duclaux showed that  $\log \eta$  bears a linear relation to the concentration  $C$ . Combining this relation with Staudinger's viscosity theory, the following equation is obtained:

$$\log K' = n.m.Km.C/2.3026 \quad (3)$$

Substituting  $\log K'$  in Equation (2) by the right-hand term of Equation (3), the following equation is obtained:

$$\log \eta = n.m.Km.C/2.3026 - n' \log P/P_0 \quad (4)$$

where  $n$  is the degree of polymerization,  $m$  is the molecular weight of the monomer,  $Km$  is a constant for each homologous series,  $C$  is the base molarity concentration, and  $n'$  is the structural viscosity index. Using the experimental data of the relative viscosity  $\eta$  under various pressures  $P$ ,  $n$  and  $n'$  can be obtained from Equation (4).

The experiments were carried out in a water thermostat at 25° C, in an ordinary Ostwald viscometer having 1.07-mm. capillary bore, which was combined with a water manostat. All experiments were carried out with 10 cc. of rubber-benzene

\* Reprinted from the *Journal of the Society of Chemical Industry, Japan*, Vol. 43, Supplemental binding No. 11, pages 359-361B, November 1940.

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solution, having almost the same concentration of 0.5 gram of rubber in 100 cc. of solution. After a series of measurements under various pressures was completed, these solutions were placed in a fused quartz flask and irradiated with ultraviolet light from a mercury vapor lamp of 1 kW. at a distance of 10 cm. from the flask. Buna-S and Perbunan could not be dissolved in benzene; however, their suspensions became clear solutions after long irradiation. The viscosity data of the rubbers before irradiation are therefore omitted in Table I.

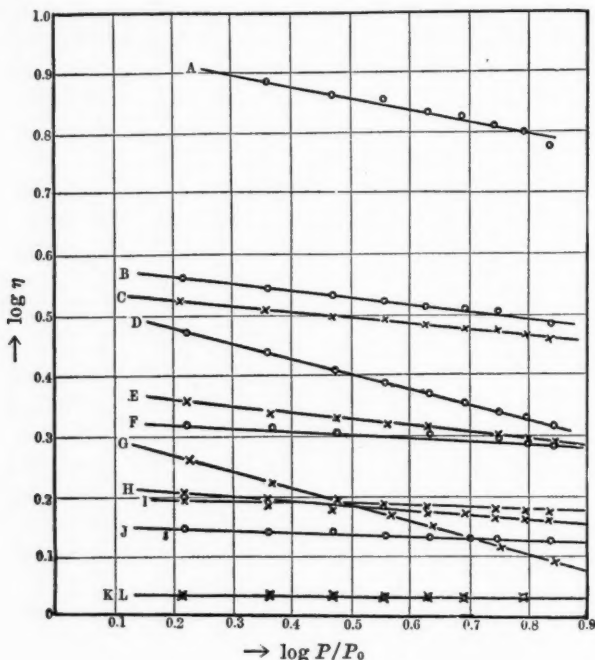


FIG. 1.

- A Pale crepe (unmasticated) before ultraviolet light irradiation.
- B Oppanol-B before irradiation.
- C Oppanol-B after 10 hrs'. irradiation.
- D Neoprene before irradiation.
- E Perbunan after 35 hrs'. irradiation.
- F Oppanol-C200 before irradiation.
- G Neoprene after 10 hrs'. irradiation.
- H Buna-S after 16 hrs'. irradiation.
- I Oppanol-C200 after 10 hrs'. irradiation.
- J Pale crepe (masticated for 40 min.) before irradiation.
- K Pale crepe (unmasticated) after 10 hrs'. irradiation.
- L Pale crepe (masticated for 40 min.) after 10 hrs'. irradiation.

These data give the straight lines as shown in Figure 1. Therefore, Equation (2) is valid.

By means of a mean-value method, the empirical equations for these straight lines were obtained. The values of  $\log K'$  and  $n'$ , calculated from the empirical equations, are tabulated in Table II. To calculate the degree of polymerization from the value of  $\log K'$ , the molecular weight of each monomer was assumed from the result of elementary analysis.  $K_m$  was calculated as  $3.0 \times 10^{-4}$ , because this constant for various kinds of synthetic rubber has not been established.



$0.6 \times 10^{-4}$  is used for the butadiene emulsion polymer<sup>2</sup> and  $3.5 \times 10^{-4}$  for the isobutylene polymer<sup>3</sup>,  $3.0 \times 10^{-4}$  being most commonly used for the natural rubber<sup>4</sup>.

From the results in Table II, the internal structure of each synthetic rubber could be judged. All synthetic rubbers show a moderate degree of polymerization; the values are, however, smaller than that of the natural rubber. The decrease in the degree due to the ultraviolet-light irradiation is much less for the synthetic rubber than for the natural rubber. Of all synthetic rubbers, Oppanol-B is most stable. Buna-S and Perbunan too seem to be very stable, though the data of unirradiated specimens are lacking. The structural viscosity indexes of natural rubber and all synthetic rubbers except Neoprene are reduced by the irradiation. The reduction is most marked for natural rubber and least for Oppanol-B. This

TABLE II

	Molecular weight of monomer	log $K'$	Degree of polymerization	$\eta'$ Structural viscosity index
Neoprene ..... Before ultraviolet light irradiation	88.5	0.52905	800	0.233
After 10 hrs'. irradiation		0.32476	500	0.278
Oppanol-B200 .... Before irradiation ....	56.0	0.58775	900	0.112
After 10 hrs'. irradiation		0.54636	840	0.102
Oppanol-C ..... Before irradiation ....	100.0	0.34457	450	0.052
After 10 hrs'. irradiation		0.20955	270	0.039
Buna-S ..... After 16 hrs'. irradiation	62.3	0.41388	570	0.062
Perbunan ..... After 35 hrs'. irradiation	53.8	0.43407	550	0.095
Pale crepe ..... (Unmasticated) before irradiation	68.0	0.96792	1490	0.207
After 10 hrs'. irradiation		0.04075	60	0.012
Pale crepe ..... (After 40 min'. mastication)	68.0	0.15846	240	0.036
Before irradiation ....		0.04158	60	0.010
After 10 hrs'. irradiation				

may be related to the workability of each rubber. The structural viscosity index of Neoprene is most remarkable, the value increasing inversely with the irradiation. It is assumed that Neoprene has a very complex structure, due to some extent to an intermixing of  $\mu$  polymer with  $\alpha$  polymer. The electron affinity of chlorine atoms in the molecule of Neoprene may be a cause of this complexity. Ultraviolet light irradiation promotes this complication. This fact is exactly analogous to the self-hardening of Neoprene during storage, which was considered as a disadvantage of this rubber, though this defect has been improved in the new type product *viz.*, Neoprene-GW. The aging properties of all synthetic rubbers are superior to those of natural rubber; the workability of synthetic rubbers is, however, generally poorer than that of natural rubber. The degree of polymerization, the structural viscosity index and the influence of ultraviolet light irradiation on these properties, as described in this paper, are sufficient to explain these facts.

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# HYCAR-OR

## PROPERTIES OF TYPICAL COMPOUNDS \*

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Hycar-OR is an oil-resistant synthetic rubber produced and sold by the Hydrocarbon Chemical and Rubber Company, which is jointly owned by The B. F. Goodrich Company and the Phillips Petroleum Company. Articles manufactured from Hycar by The B. F. Goodrich Company are sold under the trade name Ameripol. The object of this paper is to give a general view of the more important properties of a range of Hycar compounds and to illustrate the methods of compounding used. The recipes were selected, not to meet any particular specifications, but to include different types of stocks which might have commercial utility.

## RECIPES AND MIXING

The compounding of Hycar-OR differs from that of natural rubber in the use of less sulfur, more accelerator, and more softener. If these differences are borne in mind, experience gained in the compounding of natural rubber is an excellent guide to the compounding of Hycar-OR. Accelerators and pigments have approximately the same relative effects. Crude Hycar-OR contains 2 per cent of phenyl- $\beta$ -naphthylamine, which is sufficient age-resister for most purposes. For heat resistance, it is advisable to add five parts of heat-resisting antioxidants, such as AgeRite Resin D or the ketoneamine type. Resinous and tarry softeners used with natural rubber also work well with Hycar-OR. In addition, many esters, ethers and ketones used as lacquer plasticizers are valuable softeners for Hycar-OR. On the other hand, mineral and vegetable oils, fat acids, and terpene compounds are too insoluble to be useful. Table I gives the recipes of the compounds selected for this study.

Hycar-OR is tough, and does not break down on a mill to the extent that natural rubber does. The breakdown is significant, however, and for subsequent processing it must be done properly. On a 12-inch (30.5-cm.) mill this requires 5 to 10 minutes for 200 to 250 grams of Hycar-OR, with a tight mill setting. Age-resister, accelerator, and small amounts of zinc oxide may be added during the breakdown period. Softeners should be added next, preferably as a homogeneous mixture, and then pigments. Sulfur should be added last. In stocks containing channel black and only small amounts of softener, dispersion of the black is greatly improved by cooling the batch for 24 hours and then remilling for 10 minutes on a cold mill. In this case sulfur should be added during the remilling.

It is advisable to keep the cooling water on full when mixing batches of Hycar-OR because considerable heat is generated and because the best milling temperatures are approximately 120° to 140° F (49° to 60° C).

While in many cases it is possible to mix as large a batch with Hycar-OR as with natural rubber, it is generally advisable to mix somewhat smaller batches,

\* Reprinted from *Industrial and Engineering Chemistry*, Vol. 33, No. 5, pages 602-606, May 1941.

at least until the operators have gained experience. The compounds reported here were mixed in 25-pound (11.3-kg.) batches on a 60-inch (152-cm.) mill. The mixing times are given at the bottom of Table II.

TABLE I  
RECIPES OF COMPOUNDS STUDIED

Compound Type of Stock	A	B	C Gasoline hose tube	D Heat- re- sistant	E Soft	F Clay loading	G Soling	H Pure gum	I Fast- curing
Hycar-OR .....	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Zinc oxide .....	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Age-resister .....	—	—	—	5.0	—	—	—	—	—
Captax <sup>a</sup> .....	—	—	—	3.0	—	—	—	—	1.5
Altax <sup>b</sup> .....	1.25	1.0	1.0	—	1.5	1.5	1.25	1.0	—
Tuads <sup>c</sup> .....	—	—	—	3.0	—	—	—	—	—
D. O. T. G. ....	—	—	—	—	—	—	—	—	0.25
Crude lauric acid. . .	1.5	1.5	1.5	1.5	—	—	—	1.0	—
Sulfur .....	1.25	2.0	1.0	—	1.5	1.5	1.5	1.0	1.25
Channel black .....	50.0	—	—	50.0	—	—	75.0	—	50.0
Gastex .....	—	50.0	100.0	—	—	—	50.0	—	—
P-33 black .....	—	—	—	—	25.0	—	—	—	—
Clay .....	—	—	—	—	—	75.0	—	—	—
Soft coal tar. ....	3.5	—	—	10.0	—	—	25.0	—	20.0
Dibutyl phthalate ..	—	20.0	20.0	—	50.0	20.0	—	—	—
	162.50	179.5	228.5	177.5	183.0	203.0	257.75	108.0	178.00

<sup>a</sup> 2-Mercaptobenzothiazole.

<sup>b</sup> Benzothiazyl disulfide.

<sup>c</sup> Tetramethylthiuram disulfide.

<sup>d</sup> Di-*o*-tolylguanidine.

TABLE II  
PLASTICITY AND NERVE OF HYCAR COMPOUNDS

Compound	A	B	C	D	E	F	G	H	I
GOODRICH PLASTICITY									
2-lb. wt. at 100° C. ....	4.17	21.9	7.93	5.23	76.6	9.64	1.10	11.4	1.83
10-lb. wt. at 35° C. ....	2.49	16.95	8.66	3.33	74.3	9.69	1.55	7.7	2.96
10-lb. wt. at 100° C. ....	7.66	83.3	61.3	48.3	94.9	71.2	4.8	70.6	7.5
NERVE									
Percentage of length retained .....	58.2	54.0	72	55.7	47	65.2	85	35	49
Batch time (min.) ....	37	29	28	27	37	41	34	61	23
Remill time (min.) ....	10	9	7	6	9	0	8	0	9

#### PLASTICITY AND NERVE

The plasticities of the mixed stocks were determined on the Goodrich plastometer<sup>6</sup> with a 2-pound (0.9-kg.) weight at 100° C, and at 30° C and 100° C with a 10-pound (4.54-kg.) weight. The results are given in Table II.

The nerve was determined by a test found useful in this laboratory. An amount of stock equivalent to 10 grams of Hycar-OR is milled on a small mill at 100° F (37.8° C); the rolls of this mill are 4 inches (10.2 cm.) in diameter, and there is a free width of 2.5 inches (6.4 cm.) between the guides. The rolls are gradually opened until the bank just disappears. The mill is then stopped and opened wide. The batch is cut off, allowed to stand for 10 minutes at room temperature,

and then heated to about 100° C for 5 minutes. After cooling, the length,  $L$ , is measured.  $L$ , divided by the circumference of the roll and multiplied by 100, gives the percentage of length retained.

### VULCANIZATION

*Procedure.*—In moulding and vulcanizing Hycar-OR compounds, the same procedures are used as with natural rubber. In this case the rates of curing were determined on moulded strips  $4.0 \times 0.5 \times 0.025$  inch ( $10.2 \times 1.3 \times 0.06$  cm.). The time for optimum cure was selected and adjusted for the thicker test-specimens by the usual procedure for natural rubber.

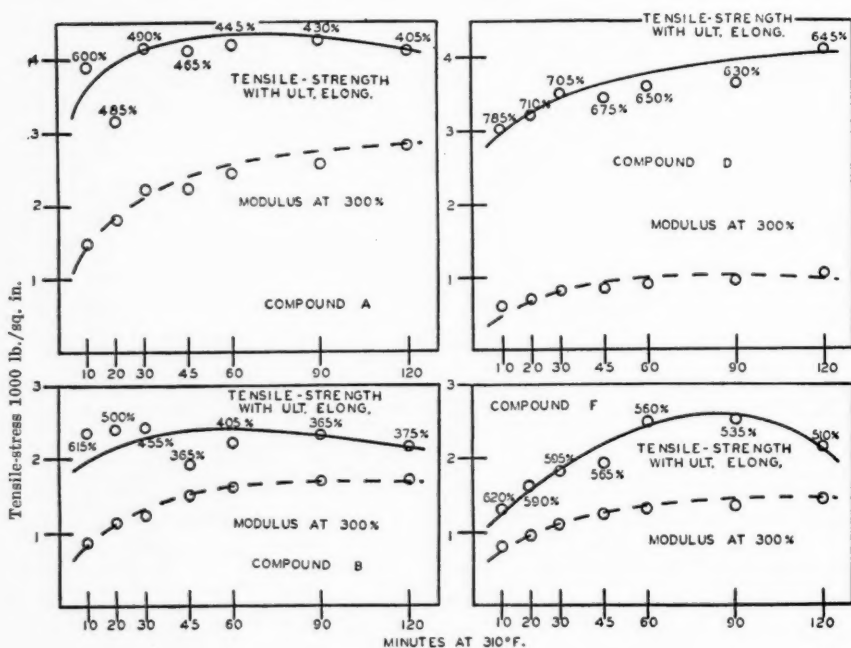


FIG. 1.—Rate of cure for compounds A, B, D, and F.

*Rate.*—Figures 1 to 4 show the change in modulus, tensile strength, and elongation with time of vulcanization at 310° F (154° C) for compounds A, B, D and F. Compound I was vulcanized at 275° F (135° C). All these compounds are flat-curing, and show little or no decrease in tensile strength with increased time of cure. Overcures are indicated by an increase in modulus and a decrease in elongation.

As in the case of natural rubber, there is probably no "best" cure for all-round performance. For most purposes, the point on the modulus curve where the slope decreases to a constant or nearly constant value should be chosen. Where low set and low hysteresis are important, a longer cure should be selected. On the other hand, aging and resistance to tearing are somewhat better at shorter cures.

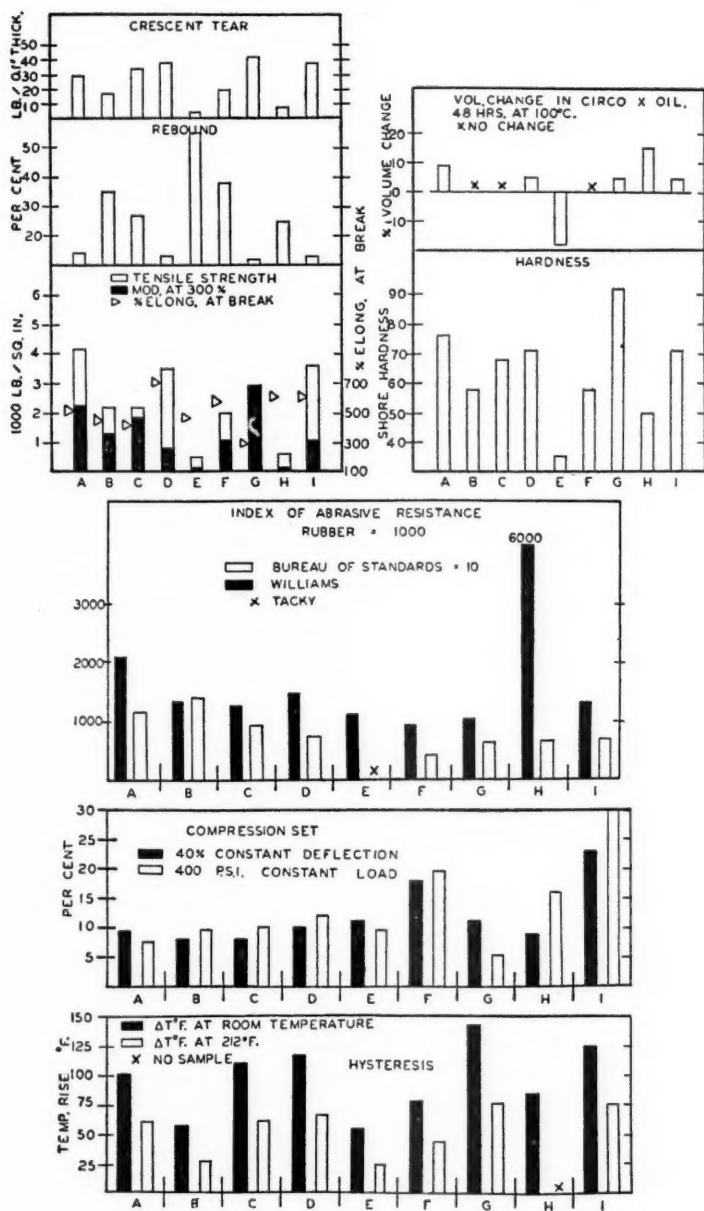


FIG. 2.—Comparison of compounds.

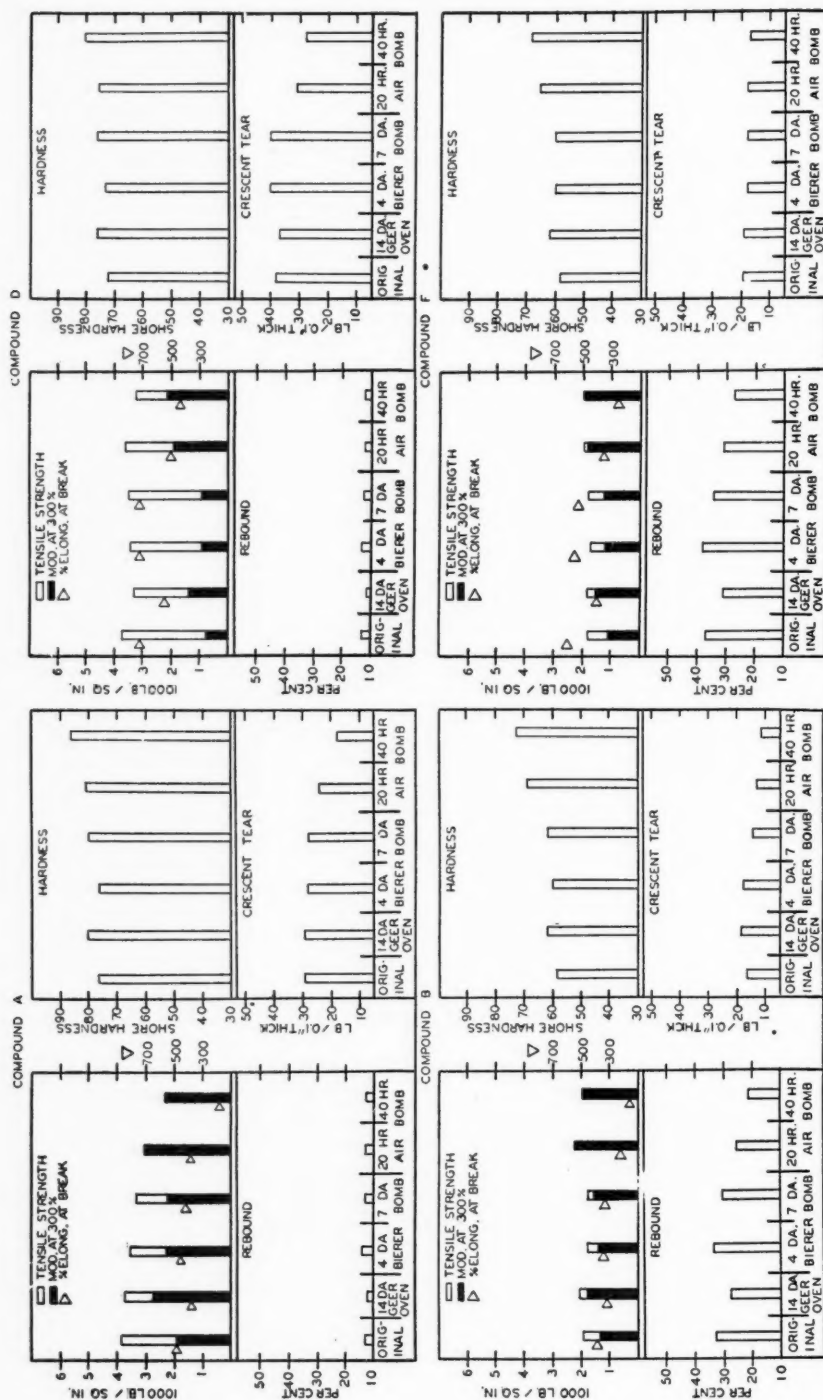


Fig. 3.—Effect of aging compounds A, B, D, and F.



## PROPERTIES OF VULCANIZED COMPOUNDS

The more important properties of the vulcanized compounds are shown in Figure 2 and in Tables III, IV and V.

Stress-strain characteristics were determined by the A. S. T. M. procedure<sup>3</sup>. Hardness was measured by a Short Durometer, Type A. Rebound was measured

TABLE III  
FLEXING LIFE OF HYCAR-OR (DE MATTIA TYPE TEST)

Compound	Flexures to failure	Compound	Flexures to failure	Compound	Flexures to failure
A	43,600	D	112,300	G	2,300
B	83,300	E	489,700	H	130,400
C	221,300	F	83,300	I	65,800

TABLE IV  
EFFECT OF SOLVENTS ON HYCAR-OR

Solvent	Per cent volume change of compound								
	A	B	C	D	E	F	G	H	I
48-HOURS' IMMERSION AT ROOM TEMPERATURE									
Hexane .....	1.5	0.0	0.0	3.0	-6.1	0.0	0.0	4.5	0.0
Benzene .....	127.4	104.8	86.1	102.4	114.7	90.7	76.3	209.6	135.4
Carbon tetrachloride....	36.8	26.0	23.4	36.8	11.7	20.8	25.1	64.3	36.8
Acetone .....	176.0	151.5	144.9	234.5	191.7	147.4	105.1	345.1	224.6
X-70 gasoline .....	4.5	1.5	3.0	4.5	-9.2	3.0	2.2	9.2	3.7
95 per cent ethanol.....	9.2	3.0	3.0	7.6	-10.0	3.0	3.0	14.9	7.6
Distilled water .....	0.0	0.0	3.0	1.5	0.75	0.0	0.75	0.0	1.5
S. A. E. 20-W oil.....	0.0	-1.5	0.0	0.75	-6.1	-0.75	0.0	0.0	0.0
95 per cent kerosene									
+5 per cent benzene	0.75	0.0	0.0	1.5	-4.5	0.0	0.0	2.2	0.0
48-HOURS' IMMERSION AT 100° C									
Circo X light oil.....	9.2	0.0	0.0	5.3	-19.1	0.0	4.5	14.9	4.5
95 per cent kerosene									
+5 per cent benzene	11.6	0.0	0.0	6.1	-17.4	18.2	6.1	0.0	4.5

TABLE V  
EFFECT OF LOW TEMPERATURES ON HYCAR-OR

Freezing Temp. (° C) with respect to:	Compound								
	A	B	C	D	E	F	G	H	I
I. Spontaneous recovery ..	0	-25	-15	+10	-30	-10	+10	-10	+10
II. Bending (light load)....	-5	-30	-30	-5	-50	-30	-5	-20	-10
III. Bending (heavy load).. <td>-15</td> <td>-35</td> <td>-35</td> <td>-15</td> <td>-55</td> <td>-40</td> <td>-10</td> <td>-30</td> <td>-15</td>	-15	-35	-35	-15	-55	-40	-10	-30	-15
IV. Brittleness .....	-55	-55	-50	-25	-55	-55	-25	-55	-40

in percentage on a modified Schopper rebound-tester. The tear data are the average of figures obtained by the transverse and longitudinal tear of crescent-shaped samples<sup>4</sup>. Compression-set was measured by both method A and method B of the A. S. T. M.<sup>2</sup>. Rapid flex hysteresis was determined by the method of Lessig<sup>7</sup>. Both methods A and B of the A. S. T. M.<sup>1</sup> were used to measure abrasion resistance. The flexing tests were run on a modified de Mattia type flex tester, with

standard dumbbell test-specimens at 100 per cent elongation and 200 flexures per minute. Immersion data were obtained by the method of Garvey<sup>6</sup>.

The freezing temperatures were determined by a method, to be described in detail later, on small tensile strips  $1.0 \times 0.5 \times 0.025$  inch. As the temperature is lowered, I is the temperature at which the specimen no longer shows rapid, spontaneous recovery. II and III are the temperatures at which it no longer bends under a light load and a heavier load, respectively. IV is the temperature at which the specimen cracks when bent  $90^\circ$ .

*Tensile strength and elongation.*—Maximum tensile strength is obtained with channel black loading (compounds A, D, and I). Semireinforcing blacks (compounds B and C), clay (compound F), magnesia, iron oxide and calcium silicate likewise give compounds with fairly good tensile strengths. High tensile strength has not been obtained in pure gum compounds (compound H). To obtain low-modulus stocks of good quality, it is necessary to use reinforcing pigments to obtain tensile strength and softeners to lower modulus. The elongation is good. It is lower with highly loaded stocks (compounds C and G) and with higher amounts of sulfur (compound B).

*Hardness.*—The hardness can be varied over a wide range by changing the type and amount of pigment and softener. Increasing the pigment loading gives harder stocks, channel black and Gastex being most effective. Increasing the amount of softener decreases the hardness, but the change depends to a large extent on the type of softener used. Lacquer plasticizers, such as dibutyl phthalate, are most effective. Coal tar and coumarone have much less effect on the hardness of cured compounds. In many cases large amounts of softener can be used.

*Schopper rebound.*—Rebound elasticity for the pure gum compound, H, is considerably lower than for rubber. Rebound is decreased by pigment loading (compounds A, D, G, and I). It is not much affected by softeners such as coal tar or coumarone, but is greatly increased by softeners such as dibutyl phthalate.

*Crescent tear.*—The best tear resistance is obtained with reinforcing pigments. Of the softeners, the resinous type has less adverse effect on tear resistance than does the dibutyl phthalate type.

*Compression-set.*—In general, these compounds have good compression-set characteristics. Compounds with the lowest sets are obtained by the use of dibutyl phthalate as a softener, semireinforcing black as a pigment, and fairly high sulfur (compound B with a slight overcure). The high set of compound F is due to the clay loading, and that of compound I is probably due to undercure.

*Hysteresis.*—Hycar-OR compounds have high hysteresis as shown by the  $\Delta T$  figures. The lowest hysteresis is obtained with the dibutyl phthalate type of softener and moderate loadings of semireinforcing blacks (compounds B and E).

*Abrasion resistance.*—In general, Hycar-OR compounds have good abrasion resistance (Figure 2). It is difficult to compare the abrasion resistance of a Hycar-OR compound with natural rubber or with other compounds of Hycar-OR, because the abrasion index depends on the test used.

*Flex resistance.*—The flex resistance (Table III) varies considerably with the type of compound. The highest number of flexures is obtained with the softest compound, E. The next softest stock, H, also has good flex resistance while the hardest stock, G, is worst. Comparisons of compound C with B and of compound D with A and I indicate that low sulfur is advantageous for flex resistance.

*Solvent resistance.*—As shown by pure gum compound H and tread-type compound A in Table IV, Hycar-OR is little affected by aliphatic or naphthenic

oils, water or alcohol. It is swelled considerably by aromatic hydrocarbons and by ketones. Carbon tetrachloride has only a small swelling action, but some of the other chlorinated hydrocarbons have a more powerful effect.

The extent of swelling in oil is lessened by pigment loading and by the use of extractable softeners. It is thus possible to compound stocks which shrink significantly, swell to a moderate extent, or show almost no change in volume in mineral oils. Where an extractable softener is used, it is advisable to select one which will not have a harmful effect on the oil.

*Cold resistance.*—While Hycar-OR compounds become logy at moderate temperatures (Table V), they maintain their flexibility well at low temperatures, and in most cases do not become brittle even at  $-50^{\circ}\text{C}$ . Pure gum compound *H* and those containing dibutyl phthalate (*B*, *C*, *E*, and *F*) are best in this respect.

*Aging and heat resistance.*—Figure 3 shows the effect of different types of aging conditions on compounds *A*, *B*, *D* and *F*. All of them stand up well in the three types of aging test, particularly heat-resistant compound *D*. The effect of aging is to decrease the elongation and, to some extent, the tensile strength, and to increase the modulus and hardness.

*Bloom.*—With the amounts of sulfur normally used with Hycar-OR, bloom is not encountered. Accelerators used in high ratio, as in compound *D*, sometimes bloom. Paraffin will bloom in 1 per cent concentration, stearic acid in 2 per cent, and mineral oil in 3-5 per cent.

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# COLD RESISTANCE OF SYNTHETIC RUBBER \*

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Automobiles must start and perform at temperatures as low as  $-40^{\circ}$  C. With the use of modern accelerators and present-day sulfur ratios, it is possible to compound natural rubber so that it will remain quite flexible at subzero temperatures.

Previously we used the T-50 test and changes in Durometer hardness as a means of determining the resistance to cold of natural and synthetic rubber parts. These measurements proved to be qualitative, but failed to show the exact characteristics desired for automobile rubber parts subject to flexing and deformation at subzero temperatures. The T-50 test also proved slow and cumbersome for checks in an automobile laboratory where speed is essential.

A modified T-50 test was tried, which consisted of elongating the measured inch of a standard tensile dumbbell from 1 to 3 inches. These samples were mounted in an apparatus (Figure 1) and placed in a room refrigerated to  $-40^{\circ}$  C. The dumbbells were then released, and the length of the marked section was measured within 30 seconds. The amount the sample failed to return in this time was expressed as per cent flexibility. This test also proved to be inconsistent and a poor measurement of the qualities sought.

The next method, termed the "drop test", consisted of measuring the time in seconds required for various rubbers to return to their original shape after the following treatment: Samples were cut from  $\frac{1}{16}$ -inch rubber sheets,  $1 \times 6$  inches long. They were clamped around the special mandrel shown in Figure 2 and allowed to "freeze" in position. The samples were then released at the upper end of the mandrel, and the time required for them to return to a horizontal position was used as an index of cold resistance. Extremely good synthetic rubber compounds return to their original shape within 0.5 second; poor samples require approximately 50-70 seconds. This test was promising, but after considerable work showed inconsistent results.

## TEST PROCEDURE

With the 1941 models, the Chrysler Corporation introduced vacuum-activated automatic transmissions. It was necessary for these transmissions to function at subzero as well as at normal or elevated temperatures. Cold-resistant measurements developed to date failed to simulate the low-temperature effects on the diaphragms used in these transmissions. As a result, we were forced to test the diaphragms themselves in the activating mechanism at  $-40^{\circ}$  C. When such tests were found to be extremely sensitive and of reproducible accuracy, it was decided to adopt this test as the standard measurement of freeze resistance in our laboratories.

In this test the activating mechanism was stripped of all the parts that were not necessary for the rubber measurements (Figure 3). The freeze resistance of the various rubber-like materials were recorded as the vacuum, in millimeters of mercury, required to reverse the diaphragm completely (Figure 4).

\* Reprinted from *Industrial and Engineering Chemistry*, Vol. 33, No. 5, pages 579-581, May 1941.

The activating mechanism and diaphragm to be tested as illustrated in Figure 3 are connected to a manometer and vacuum pump. The pump is started, and the manometer and diaphragm are observed simultaneously. At the moment when the diaphragm reverses, which happens quickly, the manometer is read. This reading gives an indication of the stiffness of the material at room temperature ( $25^{\circ}\text{C}$ ). In most cases, except those which will be referred to later, 55-65 Durometer synthetic rubber compounds reverse at room temperature between 38 and 43 mm. of mercury. The activating diaphragm assembly is then dis-

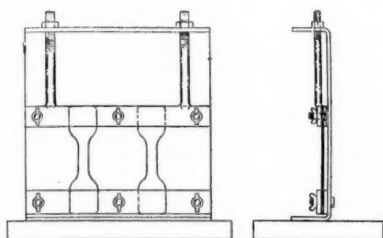


Figure 1. Apparatus for Modified T-50 Test

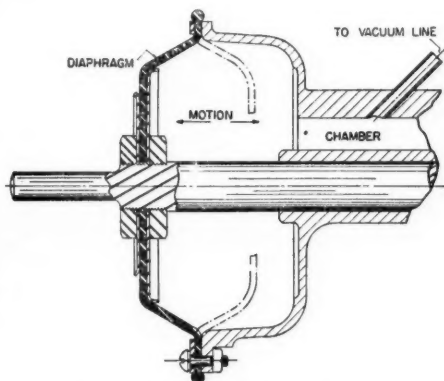


Figure 3. Activating Mechanism and Diaphragm

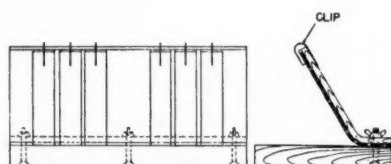


Figure 2. Apparatus for Drop Test

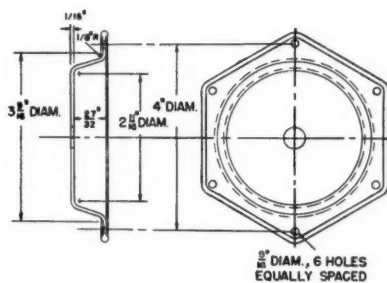


Figure 4. Details of Diaphragm for Freeze-Resistance Tests  
(Dimensions in Inches)

connected from the vacuum system, and its frictional parts are lubricated with kerosene. This prevents condensation of moisture and freezing of the frictional parts, which would give erroneous results. The assembly so treated is then placed in the cold room at  $-40^{\circ}\text{C}$  to freeze for one hour. (Previous tests indicated that most synthetic rubber compounds reach their optimum freezing characteristics after one hour; natural rubber vulcanizates require approximately 2 weeks to reach maximum hardening.) The assembly left in the cold room is reconnected to the vacuum system, which is so located that it may function outside of the cold room. The diaphragm is activated by means of vacuum, and the number of millimeters of mercury required to reverse it under these conditions is read.

TABLE I  
NEOPRENE COMPOUNDS

Material	Parts by weight			
	E	GN	PD-263	I
Neoprene Type E .....	100	—	—	—
Neoprene Type GN .....	—	100	—	—
Neoprene Type PD-263 .....	—	—	100	—
Neoprene Type I .....	—	—	—	100
Latac .....	—	0.25	—	—
Light calcined magnesia .....	10	4	10	—
FF wood rosin .....	5	—	—	—
Neozone D (phenyl- $\beta$ -naphthylamine) .....	2	2	2	2
Soft carbon black .....	30	30	30	30
Zinc oxide (New Jersey No. 2) .....	10	5	10	10
Litharge .....	—	—	—	10
Temp. of cure for 40 min., °C. ....	153	141	141	153

TABLE II  
COLD RESISTANCE OF NEOPRENE COMPOUNDS

Softener	Cold resistance, mm. of Hg.			
	E	GN	PD-263	I
Basic compound .....	620	290	133	Stiff
Barrett No. 10 .....	252	244	87	Stiff
Bardol .....	620	194	125	Stiff
Circo light-process oil .....	303	222	82	Stiff
Akroflex B (mixt. of sec. amines) .....	620	620	201	Stiff
Polar ice oil (low-freezing refrigeration oil) ..	176	148	82	Stiff
Reogen (mixt. of sulfonated petroleum products, mineral oil, and butyl alcohol) .....	176	468	62	Stiff
Synplasticizer No. 5 .....	620	252	130	Stiff
Kerosene (aniline point of 50-50 mixt., 63.3° C.) .....	277	163	125	Stiff
Dibutyl sebacate .....	77	87	36	Stiff

TABLE III  
THIOL COMPOUNDS<sup>a</sup>

Material	Parts by weight					
	E	GN	PD-263	I	—	—
Thiokol-FA .....	—	100	100	100	100	100
Thiokol-S .....	100	—	—	—	—	—
Zinc oxide .....	5	5	5	5	5	5
Altax (benzothiazyl disulfide) ..	0.5	0.5	0.5	0.5	0.5	0.5
D. P. G. (diphenylguanidine) ..	0.1	0.2	0.2	0.2	0.2	0.2
Stearic acid .....	0.5	0.5	0.5	0.5	0.5	0.5
Hard carbon black .....	30	30	45	45	45	45
Sulfur .....	1	—	—	—	—	—
Barrett No. 10 .....	—	—	15	—	—	—
Ethylene dichloride .....	—	—	15	—	—	—
Kerosene .....	—	—	—	6.3	—	—
Polar Ice Oil .....	—	—	—	—	—	9.5

<sup>a</sup> Cured 40 minutes at 148° F



## RESULTS WITH SYNTHETIC RUBBERS

Tables I to V contain the formulas of various synthetic rubber compounds tested and their freeze resistances. The rubber control-stock given in these tables is a hydraulic brake-cup material and the most freeze-resistant natural rubber compound developed in this laboratory.

To each of the basic compounds of Table I were added 15 parts of channel black and 15 parts of each (in turn) of the softeners listed in Table II. The

TABLE IV  
COLD RESISTANCE OF THIOKOL COMPOUNDS

Softener	Cold resistance (mm. Hg.)	
	Thiokol-FA	Thiokol-S
Basic compound .....	194	206
Barrett No. 10.....	87	—
Ethylene dichloride .....	214	—
Kerosene .....	143	—
Polar Ice Oil.....	151	—

TABLE V  
PHYSICAL PROPERTIES OF BEST COLD-RESISTANT COMPOUNDS

Material	Durometer hardness	Tensile, lb./sq. in.	Elongation, per cent	Modulus (300 per cent)	Dimensional change <sup>a</sup>			Cold resistance at -40° F., mm. Hg.
					96 hr., 80° F.	72 hr., 158° F.	72 hr., 250° F.	
Neoprene I + Circo light oil .....	56	1680	—	908	0	-1.71	-1.49	Stiff
Ameripol .....	55	—	—	—	—	—	—	Stiff
Thiokol-S .....	69	685	283	—	—	—	—	206
Thiokol-FA + Barrett No. 10 .....	63	827	463	654	—	—	—	87
Neoprene-GN + dibutyl sebacate .....	63	2160	675	812	-0.40	0.0	+3.23	87
Neoprene-E + dibutyl sebacate .....	52	2000	716	622	-1.70	0.48	+4.47	77
Chemigum .....	57	1870	510	—	—	—	—	74
Neoprene-PD-263 + dibutyl sebacate .....	59	1093	316	637	-2.5	-3.28	8.38	36
Natural rubber brake-cup stock .....	55	—	—	—	—	—	—	36

<sup>a</sup> In S.A.E. 20 oil (aniline point, 108° C.).

cures were the same as for the basic compounds. From the previous tests on the physical properties of these compounds, it was decided that 40 minutes at the above temperatures was the best cure for these materials. Table II gives the cold resistance of these compounds.

As discussed in the first part of this paper, 40 mm. of mercury were subtracted from the figures of Table II, IV, and V.

The relative weights of the plasticizers added to the Thiokol-FA compounds (Table III) vary. This is due to the fact that only the above amount of plasticizers could be practically milled into the given compound. From previous tests on the physical properties of these compounds, 40 minutes at 298° F was chosen as the best cure for these materials. Table IV gives the cold resistance of the compounds.

No work was done to determine the effect of various softeners on either Chemigum or Ameripol. However, sample diaphragms of both materials were tested for cold resistance. We have no information as to their chemical composition other than that they contain Chemigum and Ameripol. The latter tested "stiff," and the former, 74 mm. of mercury.

Table V contains the freeze resistance of the best cold-resistant synthetic compounds derived from results of this paper, along with the cold resistance of our natural rubber brake-cup stock.

# AN IMMERSION TEST FOR RUBBER COMPOUNDS \*

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The procedure described here was developed to determine the comparative swelling effect of a variety of liquids on a variety of compounds. To carry out such a program by the regular A. S. T. M. method<sup>1</sup> would be very expensive because of the large number of weighings and calculations.

## DESCRIPTION OF PROCEDURE

*Test specimen.*—The test-specimen is 100 mm. long and 1.6 mm. wide. The thickness may vary from 0.6 mm. to 3.0 mm. With a standard A. S. T. M. tensile sheet<sup>2</sup>, the thickness is 1.9 mm. (0.075 in.). The samples can be die-cut from any sheet of stock more than 100 mm. long and 2 mm. wide. The best procedure is to cut two strips at right angles to each other from a tensile sheet, and to take the average swell of the two strips.

An experienced operator can cut such samples to within 0.5 mm. of the exact length. With an inexperienced operator, the variation may be as much as 1.0 mm. It is desirable, therefore, to check the original length of the sample and make a correction to the increase in length,  $\Delta L$ . The correction to the original length and separate calculation of volume change,  $\Delta V$ , based on the corrected length, is not necessary because the correction to  $\Delta V$  is too small.

*Immersion tubes.*—The immersion tubes are approximately 250 mm. long, and are sealed at one end. They can be quickly and easily made from 10-mm. Pyrex tubing. In the bottom of each tube is placed a piece of 7.5-mm. glass rod about 2 cm. long, with square cut ends. This rod is for convenience in holding the tube while making readings.

These tubes can be closed with small corks or rubber stoppers if the vapor pressure of the liquid is not too high. If the tubes are to be heated, a small breather hole should be made so that the corks will not be blown out by the expanding air. Under conditions where the vapor pressure will be high, the tubes should be cooled and sealed off in a blast lamp.

Identifying numbers can be put on the corks or on aluminum tags wired to the tubes.

While 10-mm. tubes are preferred, other sizes from 8 mm. to 15 mm. can be used satisfactorily. The results will vary somewhat with the size of the tube because of the variation in the ratio of volume of solvent to volume of rubber.

*Racks for immersion tubes.*—The tubes can be placed in racks, either vertically or at an angle to the horizontal just large enough to keep the liquid from flowing out if the cork comes out. In this way a large number of tubes can be placed in a small constant temperature oven or thermostat.

*Reading table.*—The reading table (Figure 1), about a foot square and having a glass top, is set at an angle of about 15 degrees with the horizontal. Standard millimeter graph paper, marked in ink at convenient lines to facilitate reading the increase in length of the test-specimen, is fastened over the glass by means of

\* Reprinted from the *ASTM Bulletin*, No. 109, March 1941, pages 19-22.

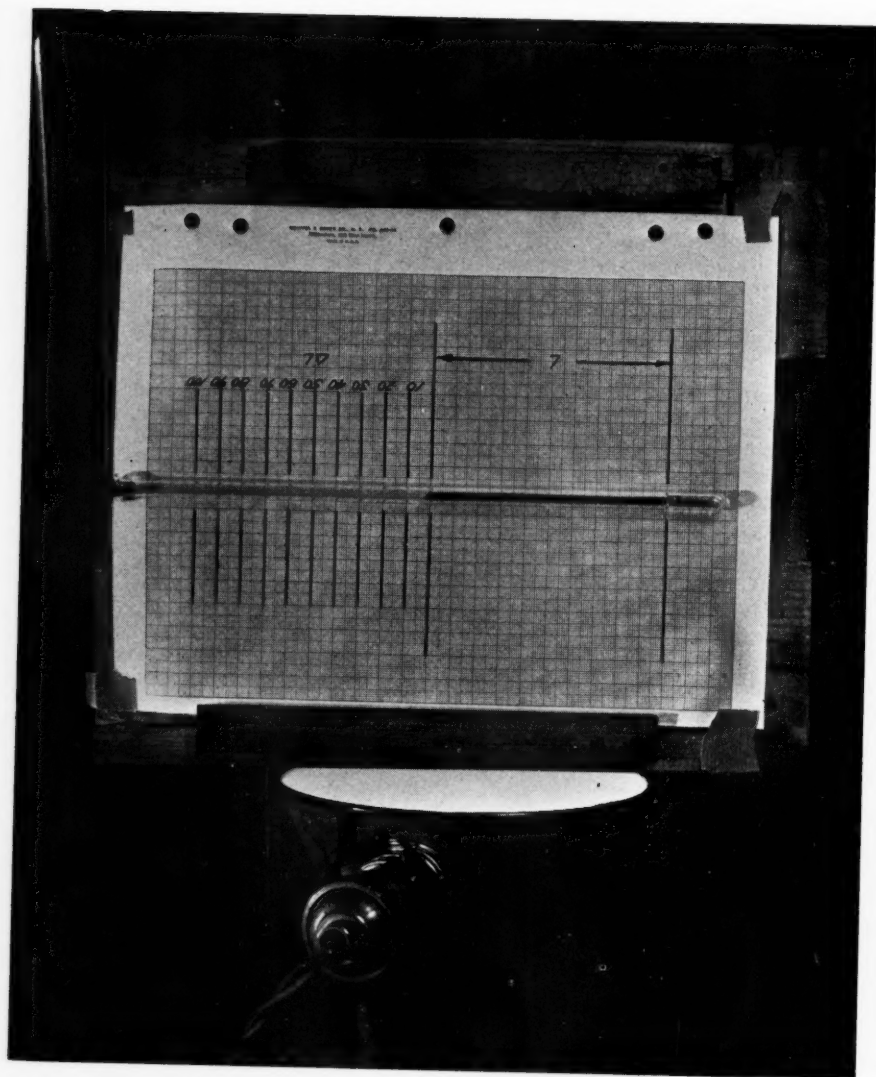


Fig. 1.—Reading table.

thumb tacks or tape. A mirror is placed under the glass at a 45-degree angle, and the light from an ordinary light bulb at the side is reflected upward through the paper. This arrangement prevents heating and consequent shrinkage of the paper.

*Operation.*—The small piece of rod is first put into the tube, and then the test-specimen. The original length of the sample is then checked, and any deviation from the standard length is applied as a correction to  $\Delta L$ . For example, if the sample length is 100.5 mm., the correction to  $\Delta L$  is  $-0.5$  mm. Next 10 cc. of liquid are added, and the tube is either corked or sealed. The tube is then kept at the specified temperature for the specified time, and then allowed to come to room temperature. The difference in length from 100.0 mm. is read to the nearest 0.5 mm. The correction to  $\Delta L$  is added to give  $\Delta L$  corrected, in millimeters. Since the original length is 100 mm.,  $\Delta L$  in mm. is also  $\Delta L$  in percentage. The corresponding  $\Delta V$  in percentage is then read directly from Table I. If more than one time of immersion is requested, the operation is repeated.

Parallax in reading the length is eliminated when the line being read goes straight across the tube as seen through the liquid. If the inked lines are drawn as shown in Figure 1, two black dots will be seen in the wall of the tube, and these should be on the corresponding line under the tube.

In some cases the test-specimen curls slightly, which may make a difference of as much as 0.5 mm. in  $\Delta L$ . A piece of small, stiff wire bent zigzag in a plane can be used to hold the sample flat if the tube is corked.

Typical results and the method of recording are given in Table II.

#### DISCUSSION OF TEST RESULTS

*Compounds used.*—Compounds RG and RT, pure-gum rubber and rubber tread, respectively, were tensile sheets cured in a press by the standard A. S. T. M. procedure. Compound RCG was a high-gum, air-curing compound, which was calendered cold to get maximum calender grain, and cured by standing at room temperature. Compounds N and P, Neoprene and Perbunan, respectively, were mixed and calendered in the factory and cured in a press.

*Effect of solvent volume on  $\Delta V$ .*—In Table III are given data obtained with three different sized tubes, together with the results secured with the standard A. S. T. M. procedure. In the 8-mm. tubes were 4.3 cc. of solvent; in the 10-mm. tubes, 10 cc.; and in the 15-mm. tubes, 25 cc. The immersions in lubricating oil were at 80° C, the others at room temperature. These results are the average of two determinations, one with the grain and one across the grain. The A. S. T. M. results are also the average of two determinations.

These results indicate that usually the volume of solvent does not have any pronounced effect but that, in some cases, notably with compound RT in lubricating oil at 80° C, it has considerable effect.

*Effect of calender grain.*—In Table IV are given the averages, for three compounds, of two determinations with the grain, two across the grain, and two by the A. S. T. M. method. These immersions were run in 8-mm. tubes at room temperature. From these results it is evident that the calender grain has a very pronounced effect on  $\Delta L$ . Part of the deviation between the new method and the A. S. T. M. method is probably due to the fact that the thickness does not change in proportion to the length. The results also indicate that there is considerable calender grain left in this sheet of compound N and very little in that of compound RT.

Since the relation between  $\Delta L$  and  $\Delta V$  in the new method is based on the assumption that swelling is isotropic, it is obvious that if the calender grain is kept at a minimum, the most satisfactory comparative results will be secured.

TABLE I  
RELATIONS OF  $\Delta L$  TO  $\Delta V$

$\Delta L$ (mm.)	$\Delta V$ (per cent)	$\Delta L$ (mm.)	$\Delta V$ (per cent)	$\Delta L$ (mm.)	$\Delta V$ (per cent)	$\Delta L$ (mm.)	$\Delta V$ (per cent)
0.5.....	1.5	25.5.....	97.5	50.5.....	240.9	75.5.....	440.1
1.0.....	3.0	26.0.....	100	51.0.....	244.3	76.....	445.2
1.5.....	4.5	26.5.....	102.4	51.5.....	247.8	76.5.....	449.8
2.0.....	6.1	27.0.....	104.8	52.....	251.2	77.....	454.5
2.5.....	7.6	27.5.....	107.2	52.5.....	254.7	77.5.....	461.2
3.0.....	9.2	28.0.....	109.7	53.....	258.2	78.....	464.0
3.5.....	10.8	28.5.....	112.2	53.5.....	261.7	78.5.....	468.8
4.0.....	12.5	29.0.....	114.7	54.....	265.2	79.....	473.5
4.5.....	14.1	29.5.....	117.2	54.5.....	268.8	79.5.....	478.3
5.0.....	15.8	30.0.....	119.7	55.....	272.4	80.....	483.2
5.5.....	17.4	30.5.....	122.2	55.5.....	276.0	80.5.....	488.1
6.0.....	19.1	31.0.....	124.8	56.....	279.6	81.....	493.0
6.5.....	20.8	31.5.....	127.0	56.5.....	283.3	81.5.....	498.0
7.0.....	22.5	32.0.....	130.0	57.....	287.0	82.....	502.9
7.5.....	24.2	32.5.....	132.6	57.5.....	290.7	82.5.....	507.9
8.0.....	26.0	33.0.....	135.3	58.....	294.4	83.....	512.8
8.5.....	27.7	33.5.....	137.9	58.5.....	298.2	83.5.....	517.9
9.0.....	29.5	34.0.....	140.6	59.....	302.0	84.....	523.0
9.5.....	31.3	34.5.....	143.3	59.5.....	305.8	84.5.....	528.1
10.0.....	33.1	35.0.....	146.0	60.....	309.6	85.....	533.2
10.5.....	34.9	35.5.....	148.7	60.5.....	313.5	85.5.....	538.3
11.0.....	36.8	36.0.....	151.5	61.....	317.3	86.....	543.5
11.5.....	38.6	36.5.....	154.3	61.5.....	321.2	86.5.....	548.7
12.0.....	40.5	37.0.....	157.1	62.....	325.2	87.....	553.9
12.5.....	42.4	37.5.....	159.9	62.5.....	329.1	87.5.....	559.2
13.0.....	44.3	38.0.....	162.8	63.....	333.1	88.....	564.5
13.5.....	46.1	38.5.....	165.7	63.5.....	337.1	88.5.....	569.8
14.0.....	48.2	39.0.....	168.6	64.....	341.1	89.....	575.1
14.5.....	50.0	39.5.....	171.5	64.5.....	345.1	89.5.....	580.5
15.0.....	52.1	40.0.....	174.4	65.....	349.2	90.....	585.9
15.5.....	54.1	40.5.....	177.3	65.5.....	353.3	90.5.....	591.3
16.0.....	56.1	41.0.....	180.3	66.....	357.4	91.....	596.8
16.5.....	58.1	41.5.....	183.3	66.5.....	361.6	91.5.....	602.3
17.0.....	60.2	42.0.....	186.3	67.....	365.7	92.....	607.8
17.5.....	62.2	42.5.....	189.3	67.5.....	369.9	92.5.....	613.3
18.0.....	64.3	43.0.....	192.4	68.....	374.2	93.....	618.9
18.5.....	66.4	43.5.....	195.5	68.5.....	378.5	93.5.....	624.5
19.0.....	68.5	44.0.....	198.6	69.....	382.7	94.....	630.1
19.5.....	70.6	44.5.....	201.7	69.5.....	387.0	94.5.....	635.8
20.0.....	72.8	45.0.....	204.9	70.....	391.3	95.....	641.5
20.5.....	75.0	45.5.....	208.0	70.5.....	395.6	95.5.....	647.2
21.0.....	77.2	46.0.....	211.2	71.....	400.0	96.....	653.0
21.5.....	79.4	46.5.....	214.4	71.5.....	404.4	96.5.....	658.8
22.0.....	81.6	47.0.....	217.7	72.....	408.8	97.....	664.5
22.5.....	83.8	47.5.....	220.9	72.5.....	413.3	97.5.....	670.3
23.0.....	86.1	48.0.....	224.2	73.....	417.8	98.....	676.2
23.5.....	88.4	48.5.....	227.3	73.5.....	422.3	98.5.....	682.1
24.0.....	90.7	49.0.....	230.8	74.....	426.8	99.....	688.1
24.5.....	93.0	49.5.....	234.1	74.5.....	431.3	99.5.....	694.1
25.0.....	95.3	50.0.....	237.5	75.....	435.9	100.....	700.0

Because the method is sensitive to calender grain, it offers an easy means of determining the extent of this grain by determining  $\Delta L$  in two directions. Comparison of the  $\Delta L$  in two directions on a tensile sheet with the  $\Delta L$  of a strip cut



TABLE II  
IMMERSION IN GASOLINE  
7 days at room temperature

Compound	$\Delta L$ (mm.)	Correction to $\Delta L$	$\Delta L$ corrected (mm.)	$\Delta V$ (per cent)
RT .....	38.0	0	38.0	162.8
	38.0	0	38.0	162.8
P .....	2.5	-0.5	2.0	6.1
	1.5	0	1.5	4.5

TABLE III  
SOLVENT VOLUME *vs.* VOLUME INCREASE

Tube size (mm.)	Ratio, volume solvent to volume rubber	Volume increase (per cent)					
		Alcohol 7 days	Hexane 7 days	Acetone 7 days	Benzene 7 days	Lubricating oil	
						7 days	14 days
Compound RT							
8 .....	11.6	3.4	142.0	—	—	251.2	333.2
10 .....	27.0	5.0	148.7	—	—	342.3	493.1
15 .....	67.5	3.0	146.0	—	—	436.1	498.5
A.S.T.M. ....	40.5	4.8	151.7	—	—	300.5	<sup>a</sup>
Compound N							
8 .....	11.6	—	—	27.3	—	52.1	60.2
10 .....	27.0	—	—	26.0	—	60.2	96.6
15 .....	67.5	—	—	23.4	—	65.4	71.8
A.S.T.M. ....	40.5	—	—	26.9	—	58.2	76.2
Compound P							
8 .....	11.6	—	—	—	130.5	—	7.6
10 .....	27.0	—	—	—	121.5	—	7.6
15 .....	67.5	—	—	—	129.1	—	9.2
A.S.T.M. ....	40.5	—	—	—	152.8	—	9.3

<sup>a</sup> Disintegrated.

TABLE IV  
CALENDER GRAIN *vs.* VOLUME INCREASE  
7 days at room temperature

Solvent	Volume increase (per cent)			
	Across grain	With grain	Average	A.S.T.M.
Compound RCG				
Acetone .....	19.1	16.4	17.8	15.6
Hexane .....	249.5	137.9	193.7	203.2
Benzene .....	365.7	200.1	282.8	302.2
Compound RT				
Alcohol .....	1.5	3.0	2.25	4.77
Hexane .....	142.0	142.0	142.0	151.7
Benzene .....	225.0	220.9	223.0	241.0
Compound N				
Acetone .....	29.5	25.1	27.3	26.9
Hexane .....	20.0	15.8	18.4	17.5
Benzene .....	211.2	165.7	188.5	200.5

from a piece of extruded tube of the same stock should give a measure of the grain left in the tube.

*Effect of thickness of the sample.*—In Table V are given data on two of the stocks sheeted and cured to different thicknesses. All of the immersions were run at room temperature in 8-mm. tubes. Some difficulty was experienced in working with the thinnest sheets by both methods. In general the differences are not great, and are probably due in part to differences in the ratio of solvent volume to rubber volume.

TABLE V  
VOLUME INCREASE *vs.* THICKNESS OF SAMPLE

Thickness (in.)	4 days at room temperature					
	Volume increase (per cent)					
	Gasoline		Benzene		Alcohol	
	Tube	A.S.T.M.	Tube	A.S.T.M.	Tube	A.S.T.M.
Compound RT						
0.017.....	193.7	164.9	277.0	277.2	2.4	5.6
0.068.....	199.5	211.3	283.7	316.6	2.7	4.3
0.114.....	190.8	211.8	226.7	300.3	2.3	3.9
Compound RG						
0.026.....	315.4	263.7	478.5	431.6	1.8	4.2
0.062.....	304.7	300.4	434.1	438.9	5.1	5.7
0.107.....	302.3	301.6	413.3	435.6	5.1	6.1

#### COMPARISON OF THE NEW METHOD WITH A.S.T.M. METHOD

*Comparison of results.*—In Table VI are given data comparing the results obtained by the new method with those obtained by the A. S. T. M. method. All results reported are the average of two determinations. In the new method the strips were cut at right angles to each other, and the immersions were run in 10-mm. tubes. Other comparative data have been given in the preceding tables.

In many cases the results are very close. In others the numerical check is not good, although it is close enough for practical purposes. For example, in a preliminary comparison of compounds for various uses the difference between a  $\Delta V$  of 3.0 and one of the 6.0 or between 218.0 and 241.0 would be of minor importance even though, as numerical checks, such results would not be considered good.

*Accuracy.*—There is a question as to which method gives the more accurate results. The greater precision of the gravimetric method is counterbalanced by the sources of error inherent in the manipulations.

*Reproducibility.*—To determine the reproducibility of results, a large number of individual results were examined to see how closely they agreed for supposedly identical determinations. Since  $\Delta L$  is read only to the nearest 0.5 mm., there are many cases where the spread in  $\Delta L$  is 0.5 mm. For a swelling of less than 50 per cent, this  $\Delta L$  value corresponds to about 1.5 to 2.0 per cent in  $\Delta V$ , whereas, for a swelling of 150 per cent, it corresponds to 3.0 per cent, and for a swelling of 400 per cent, to 4.4 per cent. Of 288 determinations, there were 14 cases where the spread between the two values of  $\Delta L$  was more than 0.5 mm. This was true in only one case where the swelling was less than 50 per cent. Of 156 determinations by the A. S. T. M. method, there was only one case where

the spread was more than 2.5 per cent and the swelling less than 50 per cent. With low swelling the checks are closer by the A. S. T. M. method. With swellings of over 50 per cent, however, there were 41 cases where the spread was over 2.5 per cent, and of these it was over 5 per cent in 24 cases and over 10 per cent in 7. With higher swellings the two methods seem about equal in reproducibility.

*Speed of operation.*—The time required for the measurements by the new method is 10 to 20 per cent of that required by the present A. S. T. M. method.

TABLE VI  
COMPARISON OF METHODS

Time of immersion (days)	Volume increase (per cent)							
	In hexane, room temperature		In benzene, room temperature		In acetone, room temperature		In lubricating oil, 80° C	
	Tube	A.S.T.M.	Tube	A.S.T.M.	Tube	A.S.T.M.	Tube	A.S.T.M.
Compound RT								
1.....	147.3	139.2	211.2	221.1	—	—	—	—
2.....	147.3	146.2	216.0	235.2	—	—	—	—
4.....	148.7	148.8	216.0	238.3	—	—	—	—
7.....	148.7	151.7	217.7	241.0	—	—	—	—
Compound RG								
1.....	—	—	—	—	21.6	20.9	256.4	223.5
2.....	—	—	—	—	22.5	20.4	288.8	251.9
4.....	—	—	—	—	18.3	20.4	351.2	288.8
7.....	—	—	—	—	18.3	20.5	446.0	368.2
14.....	—	—	—	—	—	—	<sup>a</sup>	<sup>a</sup>
Compound P								
1.....	3.0	6.0	—	—	—	—	6.1	3.7
2.....	3.0	2.6	—	—	—	—	8.5	4.2
4.....	2.3	2.0	—	—	—	—	7.7	5.7
7.....	2.3	2.0	—	—	—	—	6.1	7.9
14.....	—	—	—	—	—	—	7.6	9.3

<sup>a</sup> Disintegrated.

TABLE VII  
VOLUME INCREASE IN FREON 12

Compound	Volume increase (per cent)	
	Room temperature, 26 days	250° F, 2 days
RT .....	36.8	36.8
N .....	6.1	4.5
P .....	-1.5	-3.0

The calculations, which take as much time as the measurements by the A. S. T. M. method, are entirely eliminated. The time of the operator required for a single result is thus only 5 to 10 per cent of that required by the A. S. T. M. method.

*Difficult tests.*—Some types of immersion which are very difficult by the A. S. T. M. method are easy by the new method, for example immersion in Freon at high temperatures. In Table VII are given results of such immersions obtained by the new method. The tubes with samples in them were cooled in dry ice and the Freon 12 distilled in from a cylinder. The tubes were then

sealed in a blast lamp. They were kept at room temperature for 26 days and then at 250° F for 2 days.

*Modifications of the new procedure.*—With properly prepared tensile sheets, a single strip can be cut by an experienced operator and immersed without checking on the initial length. Such a procedure is very fast and gives fairly accurate results.

The use of two strips cut at right angles to each other and the checking of the initial length give improved accuracy and require little time.

Various possible improvements for both speed and accuracy are rather obvious. An improved method of cutting samples would eliminate the need for the initial reading. The use of tubes with flat bottoms of uniform thickness together with a suitable holder would eliminate the necessity of aligning the bottom end of the strip. A suitably mounted, movable, low-power microscope would make the readings of  $\Delta L$  more accurate. A scale made for the direct reading of  $\Delta V$  would eliminate the need for using the conversion table. All of these improvements could be incorporated into special apparatus at relatively low cost, so accurate determination would be made very rapidly.

#### CONCLUSION

The immersion procedure described here is much faster than the present A. S. T. M. method, and gives results of comparable accuracy. It requires less space and less solvent. The most serious objection to it is the occurrence of anisotropic swelling due to grain in the rubber. However, there is usually more grain in manufactured articles, such as hose, than in tensile sheets. Both methods are useful chiefly for the preliminary evaluation of compounds. The final test frequently is made on the finished article under special conditions.

The sensitivity of this test to grain effects suggests that its use with a good swelling agent will be a useful tool for measuring the extent of such grain in various compounds.

#### ACKNOWLEDGMENT

The author wishes to express his appreciation to B. M. G. Zwicker who made most of the experiments for this study.

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- <sup>2</sup> A sheet made to be tested in accordance with the Standard Methods of Sample Preparation for Physical Testing of Rubber Products (D 15-39), 1939 Book of A. S. T. M. Standards, Part III, p. 331.

## WANTED—A NEW AGING TEST \*

W. H. STEVENS

For many years rubber manufactures have been tested by artificial as well as natural aging tests. Of the former, the heat aging test by means of the Geer oven (an electric oven held at 70° C) was the first to be adopted and remains probably the widest used. The correlation between the Geer oven and natural aging varies according to the type of goods and their conditions of service, but a rough and ready guide is that one day in the oven at 70° C is approximately equivalent to six months of natural life.

Other heat-aging tests subject the rubber goods to air or oxygen at elevated temperature and pressure, with proportionate reduction of the time of test necessary for practical results.

Apart from heat, light has a great deteriorating effect on rubber and some use has been made of this in testing rubber manufactures which are subject to light aging in service.

The purpose of this article is to draw attention to the difficulty of accurately simulating natural light, particularly in reference to the conditions obtaining in direct summer sunlight, which has been found to have a far faster deteriorating action than that of ultraviolet light on rubber. For instance, it has been found that about 10 days of summer sunlight, partly deprived of its ultraviolet fraction by passage through window glass, is sufficient to completely destroy a plain rubber film which will stand up to weeks of light aging by a mercury vapor lamp or of ordinary heat aging at 70° C.

The action of light on rubber has been investigated by many experimentors<sup>1, 2, 3</sup>. Hancock<sup>4</sup> said: "the injurious effect of the sun's rays on thin films of rubber we discovered and provided against before much damage accrued." However, neither the provision which Hancock could make, nor that since made available by rubber service laboratories throughout the world, has proved adequate in the case of clear rubber films exposed to sunlight.

The normal effect of light on rubber, particularly raw rubber, is one of depolymerization. This effect may also occur with vulcanized or vulcanizable rubber. On the other hand, light can have a polymerizing effect both on raw<sup>5</sup> and vulcanized rubber. The depolymerization effect is evidenced by softening, stickiness<sup>6</sup>, and reduction of solution viscosity<sup>7</sup>. In the case of vulcanized, compounded rubbers, i.e., the rubbers of commerce, the effect of light is to produce a polymerizing effect, as shown by increasing hardness and brittleness. This effect may, however, be more or less due to progressive vulcanization as well.

Only limited use has been made of light-aging tests for rubber articles, largely because most rubber articles are opaque to light, and its action is thus confined to the surface. Henriques<sup>8</sup> appears to have been one of the first to use light in an artificial aging test, in conjunction with heat. Since then many ultraviolet lamps and "fadeometers" have been developed, largely for the paint industry, and they have been applied to rubber articles such as cables as an artificial light test<sup>9</sup>.

The view has commonly been held that the deterioration of rubber by light is due to the ultraviolet wavelengths<sup>10</sup>. Asano<sup>11</sup> investigated the action of light,

\* Reprinted from the *India-Rubber J.*, Vol. 101, No. 5, pages 87-88, February 1, 1941.

and found that exposure of a thin film (0.1 mm.) of rubber to light of wave length above 2,250 Ångstrom units yielded a transparent oxidized product.

It seems that in the past too much attention has been paid to the action of ultraviolet light. This light does not contain the wave lengths which are most damaging. It is interesting to note that in studying the Russell effect (action of volatile peroxides on a photographic plate) Van Rossem and Hessels<sup>12</sup> found that rubber exposed to visible light had greater activity than that of rubber exposed to ultraviolet light. Experiments of Davey<sup>13</sup> confirmed that ultraviolet light is not essential for the light aging of rubber.

The whole subject of the action of light on rubber has taken on a new interest as a result of the use of latex films for preventing glass splintering.

#### LATEX FOR SHATTER-PROOFING OF WINDOWS

As a result of the urgent need for transparent anti-splinter window treatments, latex compositions have been widely used for painting on the inside of windows. In this position the rubber film is protected from some of the ultraviolet wavelengths, owing to the iron, etc., content of ordinary window glass, as is well known. Despite this, the sunny weather of last summer resulted in widespread failure of the latex films on windows, through their resinification and loss of elasticity, and this despite the fact that many examples existed showing satisfactory aging throughout the previous autumn, winter and spring. Thus a few days of strong sunlight brought about a change which months of winter or spring light failed to do.

Experiments made at the time showed that compounding variations, within the limit imposed by the necessity of maintaining transparency or at least translucency, had no worth while result, despite ringing the changes of antioxidant composition and proportion. It appears that no known antioxidant will protect against light aging in transparent rubber. For example, latices of the following compositions all gave the same results, *viz.*, resinification to a degree causing total loss of extensibility in about 10 days of July sunlight.

	(Parts by weight)			
	1	2	3	4
60 per cent centrifuged latex .....	332	332	332	332
50 per cent colloidal sulfur dispersion.....	8	8	10	16
50 per cent antioxidant dispersion.....	2	2	2	4
50 per cent paraffin wax emulsion.....	—	10	—	—
15 per cent casein solution .....	15	15	15	15
50 per cent zinc oxide dispersion.....	—	—	1.0	—
50 per cent accelerator (zinc dibutylthio- carbamate) .....	—	—	2.0	—

Increasing the amount of vulcanizing ingredients or using prevulcanized latex did not improve the aging properties. Using a latex-concentrated by evaporation, however, did give better results, though still not good enough for practical purposes.

During the months of June, July and August aging tests in sunlight can be made; but they depend on the weather, which can vary widely. To standardize the test and to make it available also during the remaining nine months of the year, it was sought to duplicate the action of sunlight. Although the matter has not been pressed to a conclusion, it must be admitted that no satisfactory means has been found. A new aging test is wanted which will give the same result as



intensive sunlight passing through window glass for ten days. This new aging test should prove useful, not merely for testing latex antisplinter window treatments, but for rubber goods generally, since it is clear that none of the existing light-aging tests simulate summer conditions accurately enough<sup>14</sup>.

Experiments have been made with an enclosed carbon-arc lamp on a latex film of a composition known to fail on windows in summer time. The latex rubber film was two-thousandths of an inch thick (half that recommended for windows) and was placed directly in the light of the lamp, *i.e.*, the light did not pass through the glass first as it would in the case of a treated window. The lamp was positioned so close to the film that the temperature of the latter reached 50° C, and the intensity of the arc was said to be approximately equivalent to summer sunlight at mid-day in its blue and near ultraviolet content. After the equivalent of ten days summer sunlight the film was substantially unaffected. The worst portions only showed slight surface hardening.

By extending the period, and by the use of light filters, the surface hardening was increased slightly, and it appeared that light of a wave length of about 4,500 Ångstrom units was the most damaging. (This wave length is missing from the quartz mercury arc light.) But in no case was it found possible to produce results resembling those obtained with natural sunlight.

It appears therefore that natural sunlight contains some deteriorating wave-length bands which are not producible artificially. Some new means of light aging rubber is required and, until it is found, we shall be dependent on tests which can be made only in the three summer months.

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# ESTIMATION OF CARBON BLACK IN NEOPRENE COMPOUNDS \*

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During a recent investigation it was necessary to determine the amount of carbon black in a sample of vulcanized Neoprene. The usual method adopted for vulcanized rubber, which consists in dissolving the rubber in nitric acid (British Standard Methods of Testing Vulcanized Rubber, B.S. 903-1940, p. 28), was tried without success, as the Neoprene did not dissolve.

No methods for the analysis of Neoprene compounds appear to have been described in the literature; the following method of estimating carbon black, which has been found to work satisfactorily, may therefore prove of interest, especially as it can be used for certain other synthetic rubbers such as Buna.

About 1.0 gram of the Neoprene sample is reduced to a fine crumb, such as will pass through a B.S. 10-mesh test sieve, by means of a rapidly rotating rasp. After extraction with acetone and chloroform, the extracted material is dried in a vacuum desiccator, transferred to a 400 cc. beaker, 20 cc. of nitrobenzene added, and the whole heated on a hot plate for a few minutes to allow the Neoprene to swell. 20 cc. of 25 per cent nitric acid (25 volumes of conc. nitric acid and 75 volumes of water) are then added, and the beaker is replaced on the hot plate. The Neoprene disintegrates and dissolves in the nitrobenzene in a few minutes. The beaker is then heated on a steam bath for about an hour, after which 100 cc. of xylene is added and the mixture filtered, while hot, through an alundum crucible or prepared Gooch crucible. The carbon is carefully washed with hot xylene till free from decomposed Neoprene, and finally with acetone. After drying at 150° C, the crucible is weighed, the carbon black then burnt off in a muffle furnace, and the crucible reweighed. The difference between these weights is the amount of carbon black present.

If clay or any other filler containing combined water is also present, the combustion method described in B.S. 903-1940, p. 28, should be used to determine the amount of carbon black in the crucible.

In a series of analyses by the method above the following results were obtained:

Mixture	Nature of black	Calculated percentage	Estimated percentage
A	Micronex .....	20.5	21.6 } 21.5 } 21.4 21.2 }
B	P33 .....	29.5	29.6 } 30.0 } 29.8
C	P33 .....	32.8	33.8 } 33.2 } 33.5
D	P33 .....	22.2	23.5 } 22.0 } 22.8

The calculated percentage was obtained from the mixing formula, and will therefore be subject to small errors arising in the mixing process.

\* Reprinted from the *India-Rubber J.*, Vol. 101, No. 10, page 177, March 8, 1941.

Mixings B, C, and D contained about 1 part of sulfur per 100 parts of Neoprene as an additional vulcanizing agent; A contained no sulfur.

The method is applicable also to certain other synthetic rubbers, such as Buna S, but it does not work with Perbunan, as this does not dissolve. The following results were obtained on a Buna S compound containing Micronex:

Calculated percentage .....	26.4
Estimated percentage .....	} 27.1
	} 27.1

Although soft natural-rubber vulcanizates containing carbon black readily dissolve in the nitrobenzene-nitric acid mixture, the addition of xylene causes the liquid to gel, and so renders it difficult to filter. Other solvents seem to have the same effect.